

SEMI-EMPIRICAL POTENTIAL ENERGY CURVES

FROM SIMPLE APPROXIMATE WAVE FUNCTIONS*

by

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ABSTRACT

Semi-empirical potential energy curves for the interaction of two hydrogen atoms in the $1 \sum_g^+$ and $3 \sum_u^+$ states have been calculated by assuming a simple approximate wave function, computing the expectation value of the Hamiltonian for the system, and then considering the units of energy, e^2/α_0 , length, a_0 , and the screening parameter to be adjustable parameters, to be chosen to give as good a fit of the true curve as possible. The trial functions used were made up from 1s hydrogenic or Gaussian atomic orbitals; some allowance for polarization was included in a number of the computations. The resulting curves fail to give as faithful a representation of the true curves as had been desired. Further improvement would require the addition of undesirable complexity in the trial functions and therefore in the computations for this and for more complex systems.

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I. INTRODUCTION

Recently a number of schemes for using accurate (experimental and/or theoretical) potential energy curves for diatomic molecules to infer the characteristics of potential energy surfaces for polyatomic systems have been used for computations for H_3 and several small molecules¹⁻³. In general, these schemes have involved the estimation of molecular integrals arising from an approximate formulation of the problem in terms of relatively simple atomic orbitals.

An alternative method of semi-empiricism might take the form of choosing simple approximate wave functions for the diatomic pair, computing the diatomic potential energy curves in the usual way, forcing a fit of this computed curve to the accurately known curve by suitable adjustment of parameters and then carrying out the calculation for the polyatomic system with the parameters obtained from the diatomic calculation.

This report deals with attempts to carry out the first stage of this scheme; i.e. to choose a simple form for a trial function and to then force a fit of the accurately known potential⁴ for the \sum_g^+ and the \sum_u^+ states of H_2 . The trial functions used were (1) a scaled Heitler-London or Wang type function using scaled hydrogenic atomic orbitals, (2) a similar function using scaled Gaussian atomic orbitals, and (3) a function like (2) to which electron correlation along the internuclear axis was added in a somewhat

arbitrary fashion to improve the long range interaction behavior. In all three cases, the adjustable parameters utilized to fit the experimental data were the scaling parameter in the atomic orbitals and the so-called atomic units e^2/a_0 and a_0 . The values chosen for these constants were such as to insure that the potential resulting from a 'rigorous' computation of the binding energy expectation value with the given trial function have the correct well depth (spectroscopic dissociation energy) and equilibrium nuclear separation, with a variety of conditions used for the required third condition.

The resulting potential curves fail to give as faithful a representation of the true singlet and triplet curves as had been desired, with significant improvement seemingly dependent on the addition of (unwanted) complexity in the trial functions and therefore in the computations for complex systems.

III. CHOICE OF APPROXIMATE WAVE FUNCTIONS AND PARAMETERS

Three types of approximate wave functions have been used in the exploratory calculations which have been carried out. The first of these, ψ_H , has the form of the Wang⁵ modification of the Heitler-London function

$$\psi_H = \exp\{-Z(r_{a1} + r_{b2})\} \pm \exp\{-Z(r_{b1} + r_{a2})\} \quad (1)$$

The second, ψ_G , is of the same type except that the

$$\psi_G = \exp\{-Z^2(r_{a1}^2 + r_{b2}^2)\} \pm \exp\{-Z^2(r_{b1}^2 + r_{a2}^2)\} \quad (2)$$

hydrogenic atomic orbitals used to make up the Wang function have been replaced by simple Gaussian functions. Though it was to be expected that this substitution would lead to less accurate results than the first choice, the advantages of the use of Gaussians⁷ (primarily the far greater ease of evaluation of multicenter integrals) for the extension of the method to polyatomic systems made this function well worth investigation. In each case, the upper sign is taken for the $^1\Sigma_g^+$ state and the lower for the $^3\Sigma_u^+$ state.

From the outset it was recognized that these functions would fail to give the proper $(1/R)^6$ dependence for the long range or van der Waals potential energy. In order to introduce the electron

correlation necessary to bring about such a form at long range in as simple as possible way, the second function φ_G , was modified to give the last function φ_{GP} .

$$\begin{aligned} \varphi_{GP} = & \exp\{-z^2(r_{a_1}^2 + r_{b_2}^2)\} [1 + z^2\beta z_{a_1} z_{b_2}] \\ & \pm \exp\{-z^2(r_{b_1}^2 + r_{a_2}^2)\} [1 + z^2\beta z_{b_1} z_{a_2}] \end{aligned} \quad (3)$$

Again, the upper sign refers to the \sum_g^+ state of the molecule.

In all of these functions, the coordinate system employed is illustrated in Fig. 1. Distances are considered to be measured in units of a_0 (an adjustable parameter!) and z is an adjustable scaling or screening parameter. The parameter β , suggested by the paper of Hirschfelder and Linnett⁸, which governs the extent of electron correlation along the direction of the internuclear axis was chosen in a particular way as discussed below, and is not independent of the choice of z .

The computation of a binding energy curve for a particular trial function is represented formally by equation (4)

$$E = \frac{\langle \varphi | \mathcal{H} | \varphi \rangle}{\langle \varphi | \varphi \rangle} - \frac{\langle \varphi | \mathcal{H} | \varphi \rangle_{R=\infty}}{\langle \varphi | \varphi \rangle_{R=\infty}} \quad (4)$$

where the Hamiltonian is

$$\begin{aligned} \mathcal{H} = & -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} \\ & - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} + \frac{1}{R} \end{aligned} \quad (5)$$

This gives the curve in terms of pseudo-atomic units of energy, e^2/a_0 , and length, a_0 . These were chosen in each case to obtain for the \sum^+ state a potential minimum of the proper depth occurring at the correct internuclear separation.

A third condition is necessary to establish the value of the scaling parameter, z . A major portion of the effort has been in seeking a way of choosing this parameter to give the best possible fit of both the singlet and triplet curves.

In the case of φ_H two conditions were tried for fixing z . The first of these, referred hereafter as H1, involved requiring that the repulsive portion of the singlet curve cross the zero energy line at the proper internuclear distance. The second condition, H2, was to equate the second derivative of the singlet curve, evaluated at the potential minimum, to the force constant which is obtainable from the fundamental vibration frequency. Details are given in the following section. It will be noted that the choice of z is independent of the choice of e^2/a_0 and a_0 .

In addition, a series of calculations for arbitrary values of z ranging from 0.75 to 2.00 were carried out in order to determine

the characteristics of the potential curves obtained with a wider range of parameter values than was afforded by H1 and H2.

These calculations are labeled H2.

With φ_G the conditions imposed were as follows:

G1: entirely similar to H1.

G2: the attempt to impose the condition similar to H2 led to the conclusion that one cannot quite satisfy the condition with this trial function. The computation labeled G2 was continued with the value of z which comes closest to satisfying the condition.

G3: Since a fit of the $^3 \sum_u^+$ curve as well as the $^1 \sum_g^+$ curve was a primary goal of the investigation, one point on the actual curve may be used to "fix z ". The point used for this calculation was at the same internuclear separation for which the $^1 \sum_g^+$ state has its minimum.

Parameter choices for calculations with function φ_{GP} were made subject to the following considerations: at large R where exchange terms become unimportant because of the orthogonality of the orbitals on the different centers, it is convenient to write the Hamiltonian in terms of an atomic Hamiltonian for each atom plus a multipole expansion of the remaining terms which represent the interaction of the two atoms.⁹ Thus

$$H = H_a + H_b - \frac{1}{R^3} [2Z_{a1}Z_{b2} - X_{a1}X_{b2} - Y_{a1}Y_{b2}] + \dots \quad (6)$$

At long range the function φ_{GP} may be simplified to

$$\varphi = \exp\{-z^2(r_{a_1}^2 + r_{b_2}^2)\} [1 + z^2 \beta z_{a_1} z_{b_2}] \quad (7)$$

The interaction energy for large separations is then found to be given by (the necessary integrals were taken from work of Hirschfelder and of Kim¹⁰)

$$E = -\frac{1}{4} z \left\{ \frac{\beta}{x^{3/2}} - \beta^2 \left[\frac{1}{2} z + \frac{1}{3} \sqrt{\frac{2}{\pi}} \right] \right\} \quad (8)$$

where

$$x = z^2 R^2$$

It is immediately noticed that the desired $1/R^6$ dependence will be obtained if

$$\beta = \frac{B}{x^{3/2}} \quad (9)$$

With this choice (for comparison, see the long range form found by Hirschfelder and Linnett⁸) the energy is given by

$$E = -\frac{1}{4} \frac{z}{x^3} \left\{ B - B^2 \left[\frac{z}{2} + \frac{1}{3} \sqrt{\frac{2}{\pi}} \right] \right\} \quad (10)$$

It is apparent that this will be attractive only if

$$B > B^2 \left[\frac{1}{2} z + \frac{1}{3} \sqrt{\frac{2}{\pi}} \right]$$

and that for given x that the minimum value of the interaction energy will be obtained for

$$\beta = \frac{1}{z + \frac{a}{3} \sqrt{\frac{2}{\pi}}} \quad (11)$$

This minimum value for the energy is given by

$$E = - \frac{1}{8} \frac{z}{z + \frac{a}{3} \sqrt{\frac{2}{\pi}}} \frac{1}{x^3} \quad (12)$$

Preliminary calculations indicated that for all reasonable values of z , this long range energy is smaller in absolute magnitude than the correct $1/R^6$ dispersion energy. Therefore in the computations reported here, β was taken to have the form given by equation (9) with the constant B given as a function of z by equation (11). Primarily for reason of simplicity this form was maintained for all separations; it may be well to note that the analogous parameter in the work of Hirschfelder and Linnett⁸ exhibits considerably more complex behavior at intermediate and small separations.

The choice of the three parameters z , e^2/a_0 , and a_0 were then made as follows: for each computation, a value of z was chosen, with this choice for the calculations GP1, GP2, and GP3 being the values obtained in the calculations G1, G2, and G3, respectively. In order to restore the point of potential minimum for the singlet curve to the proper nuclear separation and depth, the

values of e^2/a_0 and a_0 from G1, G2, and G3 were then readjusted to new values. Thus GP1 is genealogically related to G1, etc. but the condition used for fixing z in the more primitive calculation is no longer satisfied.

Although one might try to formulate conditions for once again choosing z such that those physical conditions be met, the complexity of the expressions involved make this a forbidding task. It was judged more expedient to calculate potential curves for a range of arbitrarily chosen values of z , in each case first estimating e^2/a_0 , and a_0 and then readjusting these to fit the minimum of the computed curve to the true minimum. These calculations are labeled GPZ.

III. DETAILS OF THE CALCULATIONS

A. Calculations with the Hydrogenic Wang Function, φ_H .

The trial function given in equation (1) leads to the following expression for the binding energy of the molecule: (See Hirschfelder and Linnett, ref. 8)

$$E_{\pm} = \frac{e^2}{a_0} \left\{ z^2 \left[\pm \frac{Q_0 - 2S_0}{1 \pm S_0} \right] + z \left[\frac{1}{q} + \frac{U_{00}^{\pm} \pm (2S_0 - Q_0)}{1 \pm S_0} \right] \right\} \quad (13)$$

which has the form

$$E_{\pm} = \frac{e^2}{a_0} \left\{ z^2 f_{\pm}(q) + z g_{\pm}(q) \right\} \quad (14)$$

Here

$$q = \frac{zR}{a_0} \quad (15)$$

and the positive sign is taken for the singlet state, the negative sign for the triplet.

The singlet curve will have a minimum at some $q = q_0$. The condition satisfied for this point is

$$\left(\frac{dE_+}{dq} \right)_{q_0} = 0 \quad (16)$$

which serves to relate z and q_0 .

$$Z = - \left(\frac{dq_+}{dq} \right)_{q_0} / \left(\frac{df_+}{dq} \right)_{q_0} \quad (17)$$

Requiring that the minimum correspond to the experimental equilibrium separation, R_0 , $(0.74142 \text{ \AA})^4$ then fixes the parameter a_0 for any arbitrary choice of q_0 .

$$a_0 = Z R_0 / q_0 \quad (18)$$

The value of e^2/a_0 may then be chosen such that equation (14) evaluated at q_0 gives the correct binding energy, D_e .
 $(-38\,292.7 \text{ cm}^{-1})^4$.

The arbitrariness of the choice of q_0 may be removed by imposing a third condition. (In view of eqn. (17) this is equivalent to an arbitrary choice of z). In the computation H I referred to in the preceding section, the condition is to require the crossing of the zero of energy line by the repulsive section of the singlet curve to come at the proper value of $R = R_c$.
 $(0.41119 \text{ \AA})^4$. The condition is easily formulated by noting that any calculated curve will cross the $E_+ = 0$ line for some $q = q_c$.
 Then

$$q_c/q_0 = \frac{R_c}{R_0} = .554598 = 2^{15}/3^{10} \quad (19)$$

Then the condition to be satisfied is

$$E_+(q_c) = 0 = \frac{e^2}{\alpha_0} \left\{ z^2 f_+(q_c) + z g_+(q_c) \right\} \quad (20)$$

Since now $q_c = .554598 q_0$ and z is a function of q_0 through equation (17), the computation may be carried out as a search for the value of q_0 satisfying equation (20). Explicit expressions for the functions and their derivatives are given in Appendix A.

In the computation H2, as previously mentioned, the choice of q_0 (or z) is based upon the second derivative of the singlet energy curve at the minimum. From equation (13)

$$\left(\frac{d^2 E_+}{dR^2} \right)_{R_0} = \left(\frac{z}{\alpha_0} \right)^2 \frac{e^2}{\alpha_0} \left\{ z^2 \left(\frac{d^2 f_+}{dq^2} \right)_{q_0} + z \left(\frac{d^2 g_+}{dq^2} \right)_{q_0} \right\} \quad (21)$$

Upon multiplying this by R_0^2/E_0 an equation is obtained

$$\frac{R_0^2}{E_0} \left(\frac{d^2 E}{dR^2} \right)_{R_0} = \frac{q_0^2 \left\{ z^2 \left(\frac{d^2 f_+}{dq^2} \right)_{q_0} + z \left(\frac{d^2 g_+}{dq^2} \right)_{q_0} \right\}}{z^2 f_+(q_0) + z g_+(q_0)} \quad (22)$$

in which the left side contains only terms which may be related to experimental quantities and the right side is a function of q_0 only. The left side may be evaluated by writing it as

$$\frac{\mu_H R_0^2 4\pi^2 \nu_0^2}{D_e}$$

and using the values

$$D_e = 38\,292.7 \text{ cm}^{-1} \quad \text{Ref. 4}$$

$$\nu_o = 4405.3 \text{ cm}^{-1} \quad \text{Ref. 13}$$

$$\mu_H = 8.36827 \text{ gm}$$

$$R_o = 0.74142 \text{ \AA} \quad \text{Ref. 4}$$

One obtains

$$\frac{1}{D_e} \mu_H 4\pi^2 \nu_o^2 R_o^2 = -4.164696$$

The calculation H2 was carried out by conducting a numerical search for the value of q_o satisfying equation (22). Detailed expressions for the derivatives and functions needed in the computation are given in Appendix A. The fixing of a_o and e^2/a_o are completed in the same manner as described above.

The HZ Computations were relatively simple compared to those of H1 and H2. For a given value of z , arbitrary but reasonable approximations were chosen for a_o and e^2/a_o . A numerical search for the minimum in the singlet curve (Eqn. 14) was carried out; having thus established q_o , new values for a_o (Eqn. 18) and e^2/a_o (to give correct binding at the minimum) were easily obtained.

B. Calculations with the Gaussian Wang Function, φ_G

The treatment for this type of approximate wave function was analogous to that for the Hydrogenic function just discussed. The equation corresponding to (14) is

$$E_{\pm} = \frac{e^2}{a_0} \left\{ z^2 f_{\pm}(x) + z g_{\pm}(x) \right\} \quad (23)$$

where

$$x = q^2 = \frac{z^2 R^2}{a_0^2} \quad (24)$$

The expressions for $f_{\pm}(x)$ and $g_{\pm}(x)$ were obtained using integrals worked out by Hirschfelder and by Kim¹⁰. These along with expressions for the required derivatives are given in Appendix B.

The calculation for G1 was carried out exactly as described for H1 with no difficulties encountered.

The calculation for G2 failed to find a q_0 satisfying the condition expressed by equation (22). The search, which took the form of seeking a zero of the function $A(q_0) = 4.164696 - F(q_0)$ derived from equation (22), did yield the information that $A(q_0)$ has a maximum just slightly less than zero; the corresponding value of q_0 was therefore used in further computations labeled G2 for evaluation of parameters and computation of binding energy curves.

The final computation for this type of function had as its

objective the concurrent fitting of the singlet and triplet curves at an internuclear separation corresponding to the singlet minimum. This condition may be met by requiring the ratio of the calculated energies to be equal to the accurate ratio⁴; i.e., that

$$\frac{E_+}{E_-} = \frac{D_e}{D_{\text{trip}}} = \frac{-38,292.7}{47,373.6} = -.808313 \quad (25)$$

Since this calculated ratio is a function of q_0 only a search for the satisfying value of q_0 was conducted, once it was found, the parameters z , e^2/a_0 and a_0 were determined in the manner previously described.

C. Calculations with the Polarized Gaussian Functions

When the energy expression analogous to those of equations (13) or (23) is worked out for the function ψ_{GP} with B given by equation (11) for the reasons discussed in section II, the expression is considerably more complicated and cannot be put in as simple a form in the parameter z as in those earlier cases. The detailed expression is given in Appendix C.

This complexity does not greatly affect the choice of e^2/a_0 and a_0 to make the computed curve fit the singlet potential minimum, but it does make the application of a third condition for the choosing of z in the manner of the earlier calculations prohibitively difficult. However, it is relatively easy to

investigate the behavior of this potential function as a function of z by simply choosing arbitrary values of z , estimating a_0 and e^2/a_0 roughly, locating the minimum of this potential curve and then readjusting these two parameters to give the desired fit at the minimum.

IV. RESULTS

The results of these calculations are embodied in the values of the parameters obtained, which are presented in Tables I - III and in the potential energy curves plotted in Figures 2 - 16. For comparison these figures also show the accurate curves of Kolos and Wolniewicz⁴, the Morse curve for the singlet state, and an anti-Morse curve² (modified Sato function) for the triplet curve. The equations for the latter two curves are:

Morse

$${}^1E = D_1 \left\{ \exp[-2\alpha(R-R_0)] - 2\exp[-\alpha(R-R_0)] \right\} \quad (26)$$

Anti-Morse

$${}^3E = D_3 \left\{ \exp[-2\beta(R-R_0)] + 2\exp[-\beta(R-R_0)] \right\} \quad (27)$$

The values for the parameters are given in Table IV.

In the GPZ calculations, the variation of the other parameters

as the value of z is changed was obtained, the results are shown in Figures 17-19. Figure 20 gives a plot of the ratio of the coefficient of $1/R^6$ obtained in these calculation to the true value⁹ as a function of z .

V. CONCLUSIONS

As a result of this study, several rather general conclusions may be drawn:

A. The computation of potential energy curves using the trial functions here represented are relatively simple and quick to perform if a high speed computer is used. For example, a set of computations such as GPZ (as illustrated in Figures 12 - 16) involving complete singlet and triplet curves (75 points each) for nine values of z required two minutes of CDC 1604 computing time. This includes compiling time, printing time, and the search to fit the parameters, so that only a small fraction of the time was actually spent computing the curves themselves. It should also be added that little attention was given to development of the most efficient programs for these computations; if any large scale use of this method were to be made, a considerable improvement could undoubtedly be achieved.

The time required for the HZ computations was approximately the same as needed for the GPZ calculations. Although the form of the trial function and the energy expression seem simpler, the

integral evaluations involved are considerably more difficult and time consuming.

B. In overall faithfulness of representation of the Kolos and Wolniewicz⁴ curves, the polarized Gaussian Wang function, φ_{GP} , does about as well as the Hydrogenic Wang function, φ_H . The simple Gaussian Wang function, φ_G , is definitely inferior. All of the functions lead to singlet curves which exhibit too little binding in the middle range ($2.5 < R < 6.0$), in contrast to the Morse curve which fails in the opposite direction.

The triplet curves are less satisfactory, as might be expected since the parameter choice was based on the minimum of the singlet curve. The computed curves consistently give too high an energy (are too repulsive) at small separations ($R < 2.5$) and although the Polarized Gaussian form does have a van der Waals minimum at roughly the correct value of R , it is too shallow.

C. In a certain sense, the results are disappointing, particularly in the short range portion of the triplet curves and in the middle and long range portions of the singlet curves. In particular, the GPZ calculations show rather conclusively that this type of function does not contain sufficient flexibility to fit the whole range of R values and cannot be made to have the proper long range interaction.

Improvement could undoubtedly be obtained by making B a

function of R , rather than a constant, and further improvement in the long-range behavior would result from adding x and y correlation as in Hirschfelder and Linnett⁸. It is unlikely, however, that these improvements would be sufficient to compensate for the much greater complexity which would result in the computational effort required.

TABLE I

Parameters For Hydrogenic Wang Function, φ_H

	Z	a_o (A)	e^2/a_o (cm ⁻¹)
H1	1.47584689	0.659796989	1.34273729×10^5
H2	1.77499307	0.790134302	8.92062764×10^4
HZ	0.75	0.341005509	6.76993983×10^5
	1.00	0.451458951	3.30193502×10^5
	1.25	0.561149318	1.95678272×10^5
	1.50	0.670456365	1.29482548×10^5
	1.75	0.779361875	9.20257701×10^4
	2.00	0.888097438	6.87713793×10^4

TABLE II

Parameters for Gaussian Wang Function, φ_G

	Z	$a_o(\text{\AA})$	$e^2/a_o(\text{cm}^{-1})$
G1	1.21614849	0.921374110	7.60308523×10^4
G2	3.308958	2.220810	1.176088×10^4
G3	0.269293887	0.223579725	8.36352720×10^5

TABLE III

Parameters for Polarized Gaussian Wang Function, φ_{GP}

	Z	a_o (Å)	e^2/a_o (cm ⁻¹)	B
GP1	1.21614849	1.17357900	4.13027000×10^4	0.5720589
GP2	3.308958	2.747089	9.8053322×10^3	0.26035692
GP3	0.269293887	0.3026936	1.222835×10^5	1.24810118
GPZ	.500000	.546673739	8.44743682×10^4	.969064360
	.750000	.776474563	6.50564971×10^4	.780077930
	1.0	.991553328	5.07723544×10^4	.652774236
	1.25	1.20174459	4.00281044×10^4	.561191412
	1.50	1.40825854	3.20598434×10^4	.492144584
	1.75	1.61063973	2.61200967×10^4	.438226842
	2.0	1.80756696	2.16258303×10^4	.394956687
	2.25	1.99854898	1.81641543×10^4	.359463553
	2.50	2.18307460	1.54502829×10^4	.329823657

TABLE IV

Parameters for Morse and Anti Morse Functions

D_1	38292.7 cm^{-1}
D_3	15790.8 cm^{-1}
α	1.04435
β	1.000122
R_e	1.4011 au

APPENDIX A

The Functions f_{\pm} and g_{\pm} for the Hydrogenic Wang Function.
(Upper sign refers to \sum_g^+ state).

$$A-1 \quad f_{\pm}(q) = \pm \left(\frac{Q_0 - 2S_0}{1 \pm S_0} \right)$$

$$A-2 \quad g_{\pm}(q) = \frac{1}{q} - f_{\pm}(q) + \frac{U_{\infty,\infty}^{\pm}}{1 \pm S_0}$$

$$A-3 \quad \text{here } U_{\infty,\infty}^{\pm} = B_0 \pm D_0 = \frac{1}{Z} \left\{ K_{\infty,\infty} - 2G_0^{\pm} (L_{\infty,\infty} - ZQ_0) \right\}$$

The expressions for Q_0 , S_0 , B_0 and D_0 are all taken from Hirschfelder and Linnett⁸. Explicitly they are the following:

$$A-4 \quad Q_0(q) = 2 \left\{ \frac{1}{3} q^3 + \frac{4}{3} q^2 + 2q + 1 \right\} e^{-2q}$$

$$A-5 \quad S_0(q) = \left\{ \frac{1}{3} q^2 + q + 1 \right\}^2 e^{-2q}$$

$$A-6 \quad \frac{1}{Z} G_0(q) = \frac{1}{q} - \left(1 + \frac{1}{q} \right) e^{-2q}$$

$$A-7 \quad \frac{1}{Z} K_{\infty,\infty}(q) = \frac{1}{q} - \left\{ \frac{1}{6} q^2 + \frac{3}{4} q + \frac{11}{8} + \frac{1}{q} \right\} e^{-2q}$$

The explicit expression for $\frac{1}{Z} L_{\infty, \infty}$ was obtained from Pauling and Wilson¹¹

$$\text{A-8} \quad \frac{1}{Z} L_{\infty, \infty} = \frac{1}{5} \left[e^{-2q} \left\{ \frac{25}{8} - \frac{23}{4} q - 3q^2 - \frac{1}{3} q^3 \right. \right. \\ \left. \left. + 6(\gamma + \ln q) \left(\frac{1}{q} + 2 + \frac{5}{3} q + \frac{2}{3} q^2 + \frac{1}{9} q^3 \right) \right\} \right. \\ \left. + 6e^{2q} \text{Ei}(-4q) \left(\frac{1}{q} - 2 + \frac{5}{3} q - \frac{2}{3} q^2 + \frac{1}{9} q^3 \right) \right. \\ \left. - 12 \text{Ei}(-2q) \left(\frac{1}{q} - \frac{1}{3} q + \frac{1}{9} q^3 \right) \right]$$

Here $\gamma = .5772156649$ and $E_i(-x)$ is the exponential integral¹².

The derivatives needed for the calculations described were evaluated from the above expressions as follows:

1st Derivatives

$$\text{A-9} \quad \frac{df_+}{dq} = \frac{1}{1+S_0} \frac{dQ_0}{dq} - \frac{(2+Q_0)}{(1+S_0)^2} \frac{dS_0}{dq}$$

$$\text{A-10} \quad \frac{dg_+}{dq} = -\frac{1}{q^2} - \frac{df_+}{dq} + \frac{1}{(1+S_0)} \frac{dU_{\infty, \infty}}{dq} - \frac{U_{\infty, \infty}}{(1+S_0)^2} \frac{dS_0}{dq}$$

$$A-11 \quad \frac{dQ_0}{dq} = -\frac{2}{3} q e^{-2q} \{4 + 5q + 2q^2\}$$

$$A-12 \quad \frac{dS_0}{dq} = -\frac{2}{3} q e^{-2q} \left\{ \frac{1}{3} q^3 + \frac{4}{3} q^2 + 2q + 1 \right\}$$

$$A-13 \quad \frac{dU_{\infty,\infty}^+}{dq} = \frac{1}{z} \left\{ \frac{dK_{\infty,\infty}}{dq} - 2 \frac{dG_0}{dq} + \frac{dL_{\infty,\infty}}{dq} - z \frac{dQ_0}{dq} \right\}$$

$$A-14 \quad \frac{1}{z} \frac{dK_{\infty,\infty}}{dq} = -\frac{1}{q^2} + e^{-2q} \left\{ \frac{1}{3} q^2 + \frac{7}{6} q + 2 + \frac{2}{q} + \frac{1}{q^2} \right\}$$

$$A-15 \quad \frac{1}{z} \frac{dG_0}{dq} = -\frac{1}{q^2} + e^{-2q} \left\{ 2 + \frac{2}{q} + \frac{1}{q^2} \right\}$$

$$A-16 \quad \frac{1}{z} \frac{dL_{\infty,\infty}}{dq} = \frac{1}{5} \left[\begin{aligned} & e^{-2q} \left\{ 12 + \frac{11}{2} q + 5q^2 + \frac{2}{3} q^3 \right. \\ & \quad \left. + 6(\gamma + \ln q) \left(-\frac{1}{q^2} - \frac{2}{q} - \frac{7}{3} - 2q \right) \right. \\ & \quad \left. \left. - q^2 - \frac{2}{9} q^3 \right) \right. \\ & \quad + 6e^{2q} Ei(-4q) \left\{ -\frac{1}{q^2} + \frac{2}{q} - \frac{7}{3} + 2q - q^2 + \frac{2}{9} q^3 \right\} \\ & \quad \left. + 12 Ei(-2q) \left\{ \frac{1}{q^2} + \frac{1}{3} - \frac{1}{3} q^2 \right\} \right] \end{aligned} \right]$$

2nd Derivatives

A-17

$$\frac{d^2 f_+}{dq^2} = \left\{ \begin{aligned} & \frac{1}{1+S_0} \frac{d^2 Q_0}{dq^2} - \frac{2}{(1+S_0)^2} \frac{dS_0}{dq} \frac{dQ_0}{dq} \\ & - \frac{(2+Q_0)}{(1+S_0)^2} \frac{d^2 S_0}{dq^2} + 2 \frac{(2+Q_0)}{(1+S_0)^3} \left(\frac{dS_0}{dq} \right)^2 \end{aligned} \right\}$$

A-18

$$\frac{d^2 g_+}{dq^2} = \left\{ \begin{aligned} & \frac{2}{q^3} - \frac{d^2 f_+}{dq^2} + \frac{1}{1+S_0} \frac{d^2 U_{\infty,\infty}^+}{dq^2} \\ & - \frac{2}{(1+S_0)^2} \frac{dS_0}{dq} \frac{dU_{\infty,\infty}^+}{dq} - \frac{U_{\infty,\infty}^+}{(1+S_0)^2} \frac{d^2 S_0}{dq^2} \\ & - \frac{2 U_{\infty,\infty}^+}{(1+S_0)^3} \left(\frac{dS_0}{dq} \right)^2 \end{aligned} \right\}$$

A-19

$$\frac{d^2 Q_0}{dq^2} = -\frac{4}{3} e^{-2q} \left\{ 2 + q - 2q^2 - 2q^3 \right\}$$

A-20

$$\frac{d^2 S_0}{dq^2} = \frac{2}{3} e^{-2q} \left\{ \frac{2}{3} q^4 + \frac{4}{3} q^3 - 2q - 1 \right\}$$

A-21

$$\frac{d^2 U_{\infty,\infty}^+}{dq^2} = \frac{1}{\pi} \left\{ \frac{d^2 K_{\infty,\infty}}{dq^2} - 2 \frac{d^2 G_2}{dq^2} + \frac{d^2 L_{\infty,\infty}}{dq^2} - 2 \frac{d^2 Q_0}{dq^2} \right\}$$

A-22

$$\frac{1}{z} \frac{d^2 K_{\infty\infty}}{dq^2} = \frac{2}{q^3} - \left[\frac{2}{3} q^2 + \frac{5}{3} q + \frac{17}{6} + \frac{4}{q} + \frac{4}{q^2} + \frac{2}{q^3} \right] e^{-2q}$$

A-23

$$\frac{1}{z} \frac{d^2 G_0}{dq^2} = \frac{2}{q^3} - 2 \left(\frac{1}{q^3} + \frac{2}{q^2} + \frac{2}{q} + 2 \right) e^{-2q}$$

A-24

$$\frac{1}{z} \frac{d^2 L_{\infty\infty}}{dq^2} = \frac{1}{5} \left[e^{-2q} \left\{ -\frac{24}{q} - \frac{37}{2} - 17q - 8q^2 - \frac{4}{3}q^3 \right\} + 12(\gamma + \ln q) \left(\frac{1}{q^3} + \frac{2}{q^2} + \frac{2}{q} + \frac{4}{3} \right) + q + \frac{2}{3}q^2 + \frac{2}{9}q^3 \right] + 12e^{2q} Ei(-4q) \left\{ \frac{1}{q^3} - \frac{2}{q^2} + \frac{2}{q} - \frac{4}{3} + q - \frac{2}{3}q^2 + \frac{2}{9}q^3 \right\} - 24 Ei(-2q) \left\{ \frac{1}{q^3} + \frac{1}{3}q \right\}$$

APPENDIX B

The functions f_{\pm} and g_{\pm} for the Gaussian Wang function.
 (Upper + sign refers to \sum_g^{+} state).

$$B-1 \quad f_{\pm}(x) = \frac{x}{e^x \pm 1}$$

which, for the sake of convenience in computation may be written as

$$B-2 \quad f_{\pm}(x) = x f'_{\pm}(x)$$

$$B-3 \quad \text{with } f'_{\pm}(x) = (e^x \pm 1)^{-1}$$

It will be noted that this appears in the expression for g_{\pm}

$$B-4 \quad g_{\pm}(x) = \frac{1}{\sqrt{x}} + \frac{2}{\sqrt{\pi}} f'_{\pm}(x) h_{\pm}(x)$$

$$B-5 \quad \text{where } h_{\pm}(x) = -(2\sqrt{2} + 1) + 4\sqrt{2} F\left(\frac{x}{2}\right) \\ \pm e^x \{2\sqrt{2} F(2x) - F(x)\}$$

$$B-6 \quad F(x) = \frac{1}{2} \sqrt{\frac{\pi}{x}} \operatorname{erf}(\sqrt{x})$$

where $\operatorname{erf}(Z)$ is the error function.¹¹

1st Derivatives

$$B-7 \quad \frac{df_+}{dq} = 2\sqrt{x} \left\{ f'_+(x) + x \frac{df'_+}{dx} \right\}$$

$$B-8 \quad \frac{dg_+}{dq} = 2\sqrt{x} \left\{ -\frac{1}{2} x^{-\frac{3}{2}} + \frac{2}{\sqrt{\pi}} \left[f'_+(x) \frac{dh_+}{dx} + h_+(x) \frac{df'_+}{dx} \right] \right\}$$

$$B-9 \quad \frac{df'_+}{dx} = e^x \left\{ f'_+(x) \right\}^2$$

$$B-10 \quad \frac{dh_+}{dx} = \frac{1}{2x} \left\{ 8\sqrt{2} \left[e^{-x/2} - F\left(\frac{x}{2}\right) \right] + \sqrt{2} e^{-x} - 1 \right. \\ \left. + e^x \left[\sqrt{2} (4x-1) F(2x) - (2x-1) F(x) \right] \right\}$$

2nd Derivatives

$$B-11 \quad \frac{d^2 f_+}{dq^2} = 2 \left\{ f'_+(x) + 5x \frac{df'_+}{dx} + 2x^2 \frac{d^2 f'_+}{dx^2} \right\}$$

$$B-12 \quad \frac{d^2 g_+}{dq^2} = 4x \frac{d^2 g_+}{dx^2} + 2 \frac{dg_+}{dx}$$

$$B-13 \quad \frac{d^2 f'_+}{dx^2} = e^x [f'_+(x)]^2 [1 + 2f'_+(x)e^x]$$

$$B-14 \quad \frac{d^2 h_+}{dx^2} = \frac{1}{2x^2} \left\{ \begin{aligned} &\frac{3}{2} - x - \frac{5}{4}\sqrt{2}e^{-x} - 4\sqrt{2}(4+x)e^{-\frac{x}{2}} \\ &+ 16\sqrt{2}F\left(\frac{x}{2}\right) + e^x \left[\sqrt{2}(4x^2 - \right. \\ &\left. 2x + \frac{5}{4})F(2x) - (2x^2 - 2x + \frac{3}{2})F(x) \right] \end{aligned} \right\}$$

APPENDIX C

Binding energy expression, Gaussian Wang with simple polarization

$$\begin{aligned}
 \text{C-1} \quad E_{\pm}(x) = \frac{e^2}{a_0} & \left\{ \begin{aligned} & \left[T_{11}(x) + 2\beta' T_{12}(x) + \beta'^2 T_{22}(x) \right] z^2 \\ & + \left[\begin{aligned} & VNA_{11}(x) + 2\beta' VNA_{12}(x) + \beta'^2 VNA_{22}(x) \\ & + VER_{11}(x) + 2\beta' VER_{12}(x) + \beta'^2 VER_{22}(x) \\ & + RN_{11}(x) + 2\beta' RN_{12}(x) + \beta'^2 RN_{22}(x) \end{aligned} \right] z \end{aligned} \right\} \\
 & \frac{1 + \frac{1}{16}\beta'^2 \pm e^{-x} \left\{ 1 - \frac{1}{2}\beta' x + \frac{1}{16}(1-x)^2 \beta'^2 \right\}}{
 \end{aligned}$$

$$- \frac{e^2}{a_0} \left\{ 3z^2 - 4\sqrt{\frac{2}{\pi}} z \right\}$$

Here

$$\text{C-2} \quad x = \frac{z^2 R^2}{a_0^2}$$

$$C-3 \quad \text{and} \quad \beta' = \beta/z^2 = B/x^{3/2}$$

and in the computations, the constant B is given by
(see eqn. 24 and preceding discussion).

$$C-4 \quad B = (z + \frac{2}{3} \sqrt{\frac{2}{\pi}})^{-1}$$

The remaining quantities in C-1 are given by the following expressions, with the upper sign taken for the \sum_g^+ state and the lower sign for the \sum_u^+ state.

$$C-5 \quad T_{11}(x) = 3 \left\{ 1 \pm e^{-x} \left(1 - \frac{x}{3} \right) \right\}$$

$$C-6 \quad VNA_{11}(x) = -4\sqrt{\frac{2}{\pi}} \left\{ 1 + F(2x) \pm 2F\left(\frac{x}{2}\right) e^{-x} \right\}$$

$$C-7 \quad VER_{11}(x) = \frac{2}{\sqrt{\pi}} \left\{ F(x) \pm e^{-x} \right\}$$

$$C-8 \quad RN_{11}(x) = \frac{1}{\sqrt{x}} \left\{ 1 \pm e^{-x} \right\}$$

$$C-9 \quad T_{1a}(x) = \pm \frac{1}{4} x(x-5) e^{-x}$$

$$C-10 \quad VNA_{1a}(x) = \pm 2\sqrt{\frac{2}{\pi}} \left\{ e^{-\frac{x}{2}} + (x-1)F\left(\frac{x}{2}\right) \right\} e^{-x}$$

$$C-11 \quad VER_{1a}(x) = \frac{1}{4\sqrt{\pi}} \left\{ \frac{1}{x} [(1+x)e^{-x} - F(x)] \right. \\ \left. \pm \frac{1}{3}(1-6x)e^{-x} \right\}$$

$$C-12 \quad RN_{1a}(x) = \mp \frac{1}{4} \sqrt{x} e^{-x}$$

$$C-13 \quad T_{2a}(x) = \frac{1}{16} \left\{ 5 \pm e^{-x}(1-x)(5-8x+x^2) \right\}$$

$$C-14 \quad VNA_{2a}(x) = -\sqrt{\frac{2}{\pi}} \left\{ \begin{aligned} &\frac{1}{6} + \frac{1}{8}x(1+2x)[F(2x) - e^{-2x}] \\ &\pm \frac{1}{x}(1-x)\left[\left(1+\frac{x}{2}-\frac{x^2}{2}\right)F\left(\frac{x}{2}\right) \right. \\ &\quad \left. - \left(1+\frac{1}{2}x\right)e^{-\frac{x}{2}} \right] e^{-x} \end{aligned} \right\}$$

$$C-15 \quad VER_{2a}(x) = \frac{1}{8\sqrt{\pi}} \left\{ \begin{aligned} &\frac{1}{2} \left[\left(2 + \frac{2}{x} + \frac{3}{x^2}\right)F(x) \right. \\ &\quad \left. - \left(x + \frac{5}{2} + \frac{4}{x} + \frac{3}{x^2}\right)e^{-x} \right] \\ &\pm \left(\frac{49}{60} - \frac{5x}{3} + x^2 \right) e^{-x} \end{aligned} \right\}$$

$$C-16 \quad RN_{2a}(x) = \frac{1}{16\sqrt{x}} \left\{ 1 \pm (1-x)^2 e^{-x} \right\}$$

REFERENCES

1. F. O. Ellison, N. T. Huff, and J. C. Patel, J. Am. Chem. Soc. 85, 3544 (1963).
2. R. N. Porter and M. Karplus, J. Chem. Phys. 40, 1105 (1964).
3. J. K. Cashion and D. R. Herschbach, J. Chem. Phys. 40, 2358 (1964).
4. W. Kolos and L. Wolniewicz, J. Chem. Phys. 43, 2429 (1965).
5. S. C. Wang, Phys. Rev. 31, 579 (1928).
6. W. Heitler and F. London, Z. F. Phys. 44, 455 (1927).
7. C. M. Reeves and R. Fletcher, J. Chem. Phys. 42, 4073 (1965).
8. J. O. Hirschfelder and J. W. Linnett, J. Chem. Phys. 18, 130 (1950).
9. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, The Molecular Theory of Gases and Liquids, John Wiley and Sons, New York, 1954, page 922.
10. H. J. Kim, University of Wisconsin Theoretical Chemistry Institute Technical Report WIS-TCI-0000, Jan. 1967.
11. Linus Pauling and E. Bright Wilson, Introduction to Quantum Mechanics, McGraw-Hill, New York, 1935, p. 343.
12. Handbook of Mathematical Functions, U. S. Dept. of Commerce, National Bureau of Standards, Applied Mathematics series 55 (1964).
13. G. Herzberg, Molecular Spectra and Molecular Structure I. Diatomic Molecules, Prentice-Hall, New York, 1939.

CAPTIONS FOR FIGURES

Figure	Caption
1.	The coordinate system used in these calculations
2-3.	Fitted singlet curves resulting from Wang type trial functions with hydrogenic orbitals. For comparison, the exact curve as computed by Kolos and Wolniewicz (ref. 4) and the familiar Morse potential are plotted also.
4-6.	Fitted triplet curves resulting from Wang type trial functions with hydrogenic orbitals. For comparison the exact curve as computed by Kolos and Wolniewicz (ref. 4) and an "anti-Morse potential" (ref. 2) are plotted also.
7.	Fitted singlet and triplet curves resulting from Wang type trial functions with hydrogenic orbitals and with arbitrary values of the screening parameter z .
8.	Fitted singlet curves resulting from Wang type trial functions with Gaussian orbitals.
9.	Fitted triplet curves resulting from Wang type trial functions with Gaussian orbitals.
10.	Fitted singlet curves resulting from trial functions which include polarization; Gaussian orbitals.
11.	Fitted triplet curves resulting from trial functions which include polarization; Gaussian orbitals.
12-13.	Fitted singlet curves resulting from trial functions which include polarization, Gaussian orbitals; arbitrarily chosen values for the screening parameter.

Captions, continued

- 14-16. Fitted triplet curves resulting from trial functions which include polarization, Gaussian orbitals; arbitrarily chosen values for the screening parameter.
17. Variation of the energy parameter e^2/a_0 with the screening parameter z for polarized Gaussian trial functions.
18. Variation of the length parameter a_0 with the screening parameter z for polarized Gaussian trial functions.
19. Variation of the optimum polarization constant B with the screening parameter z for polarized Gaussian trial functions.
20. Ratio of the long range energy calculated with polarized Gaussian trial functions and arbitrary values of z to the correct London dispersion energy.

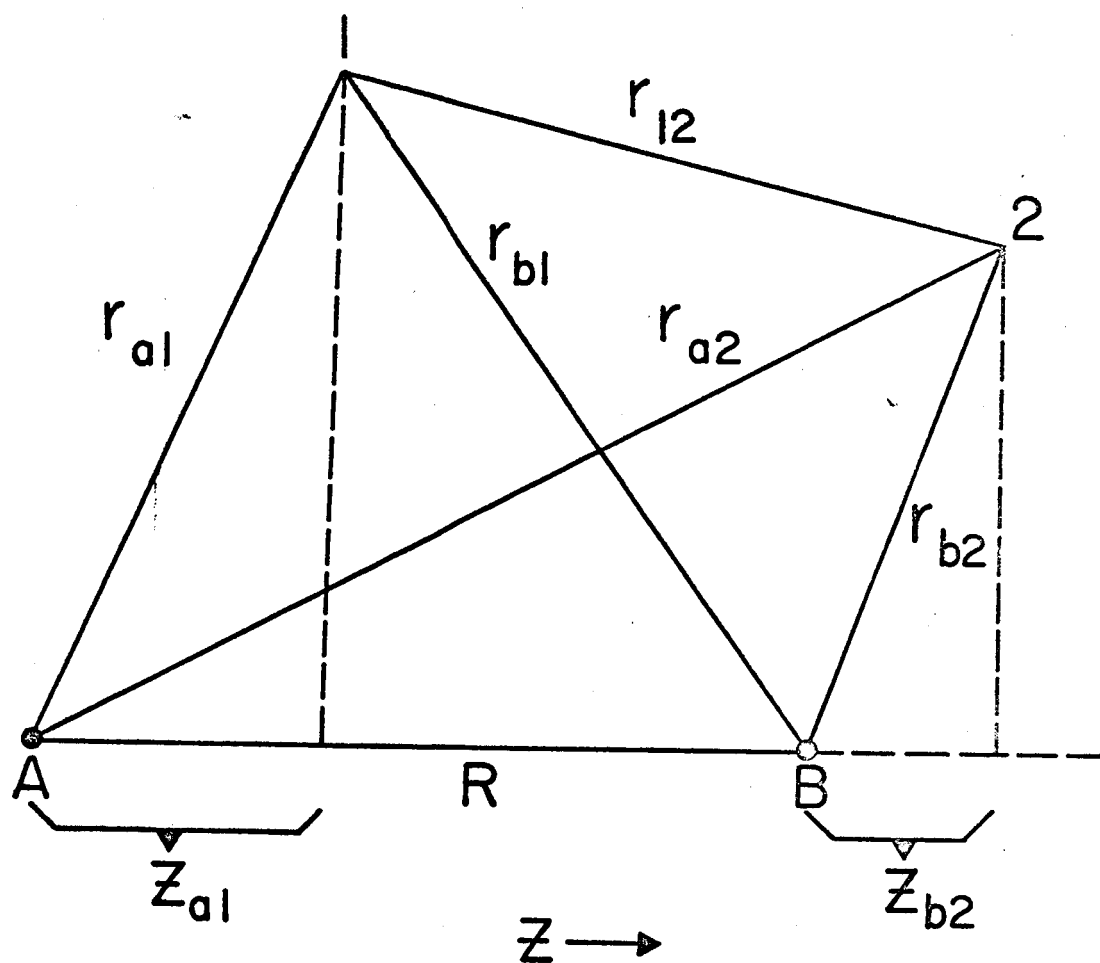


Figure 1

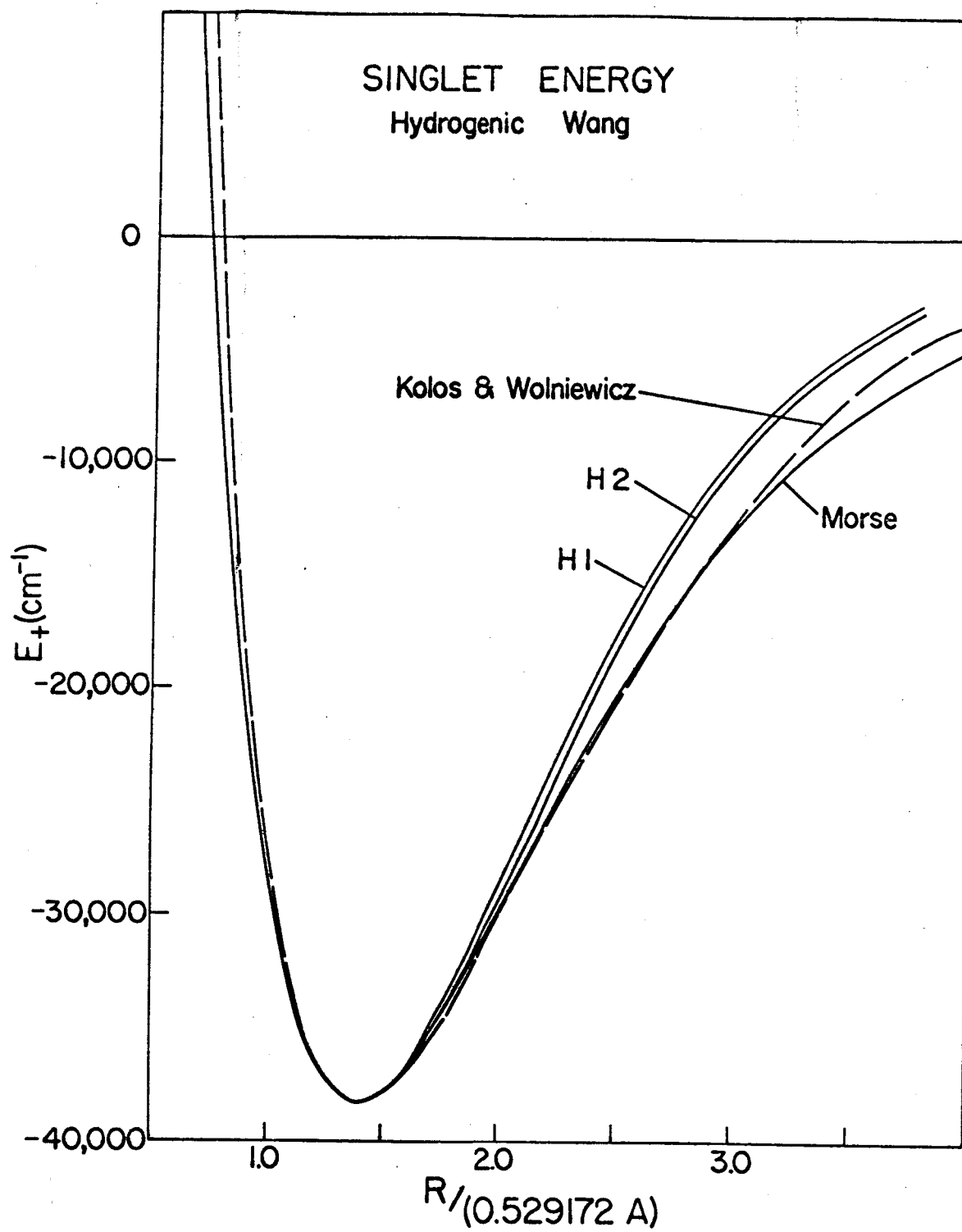


Figure 2

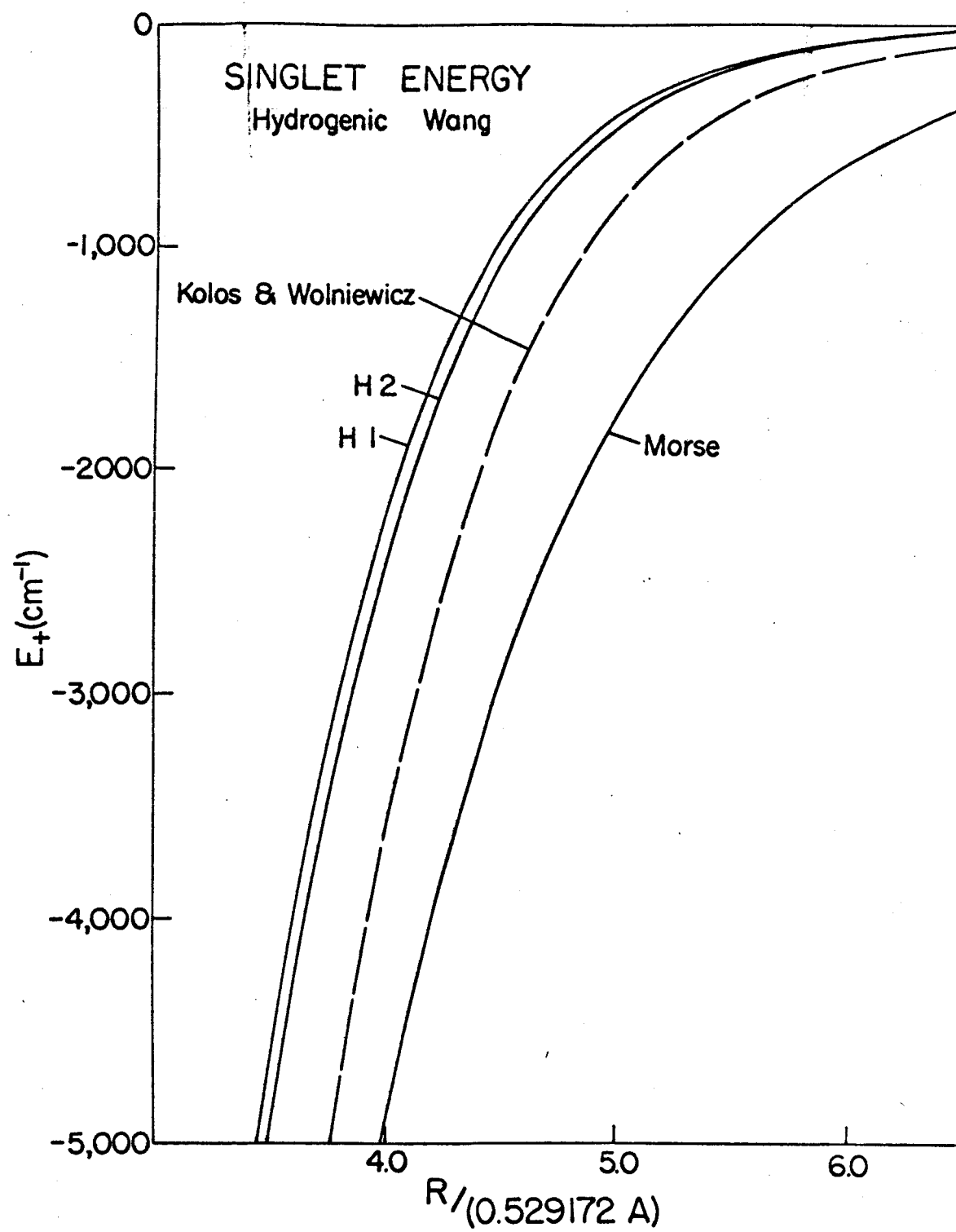


Figure 3

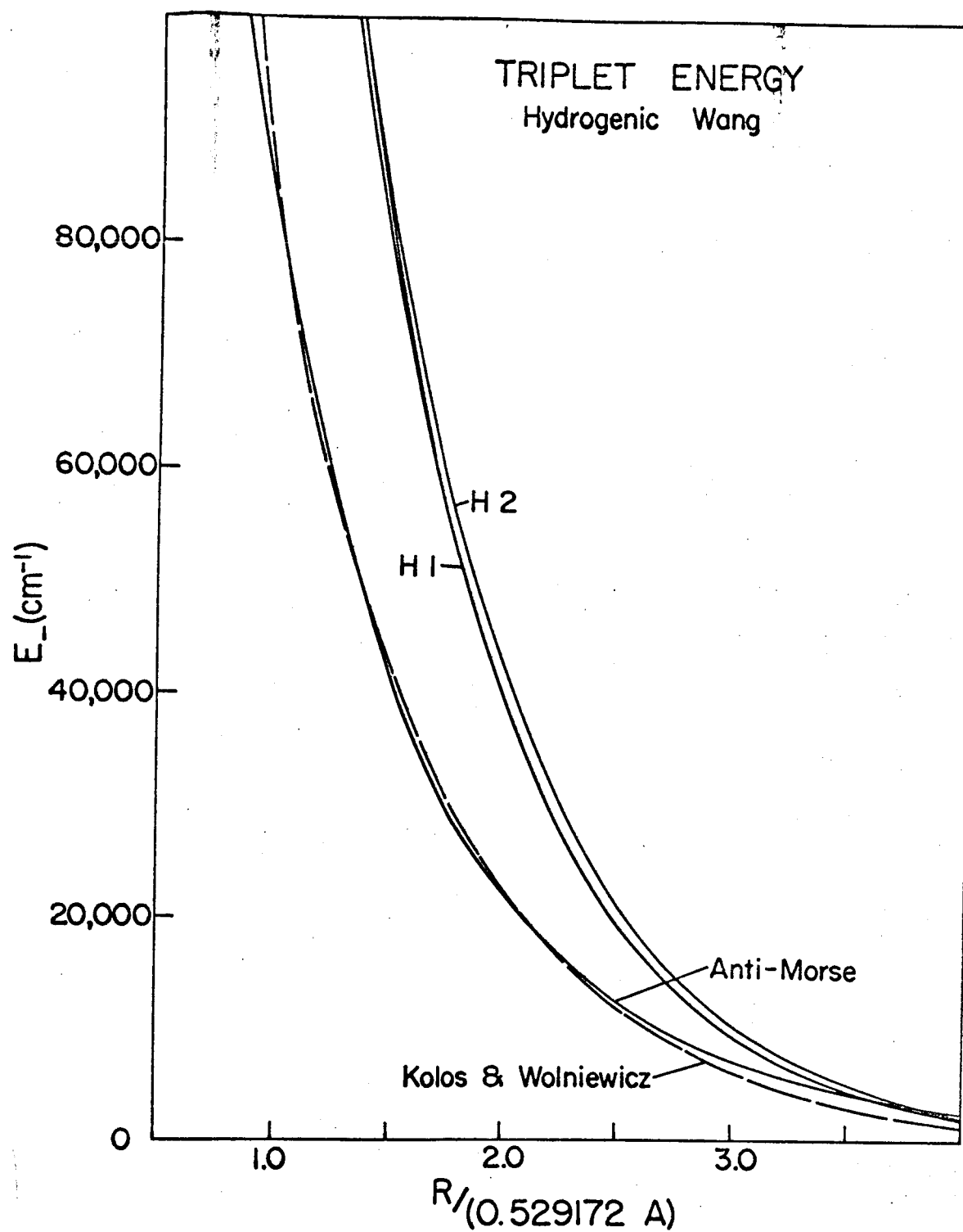


Figure 4

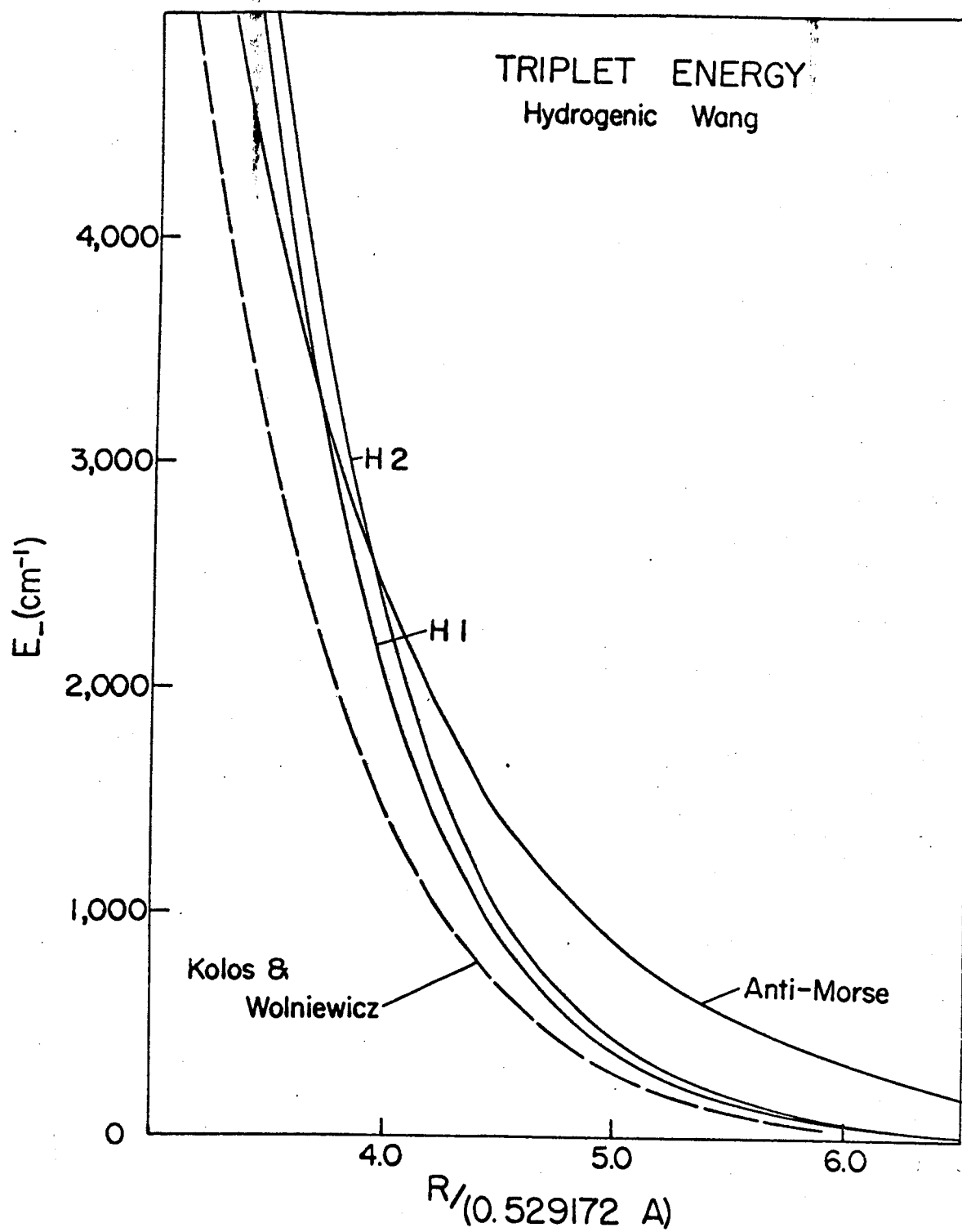


Figure 5

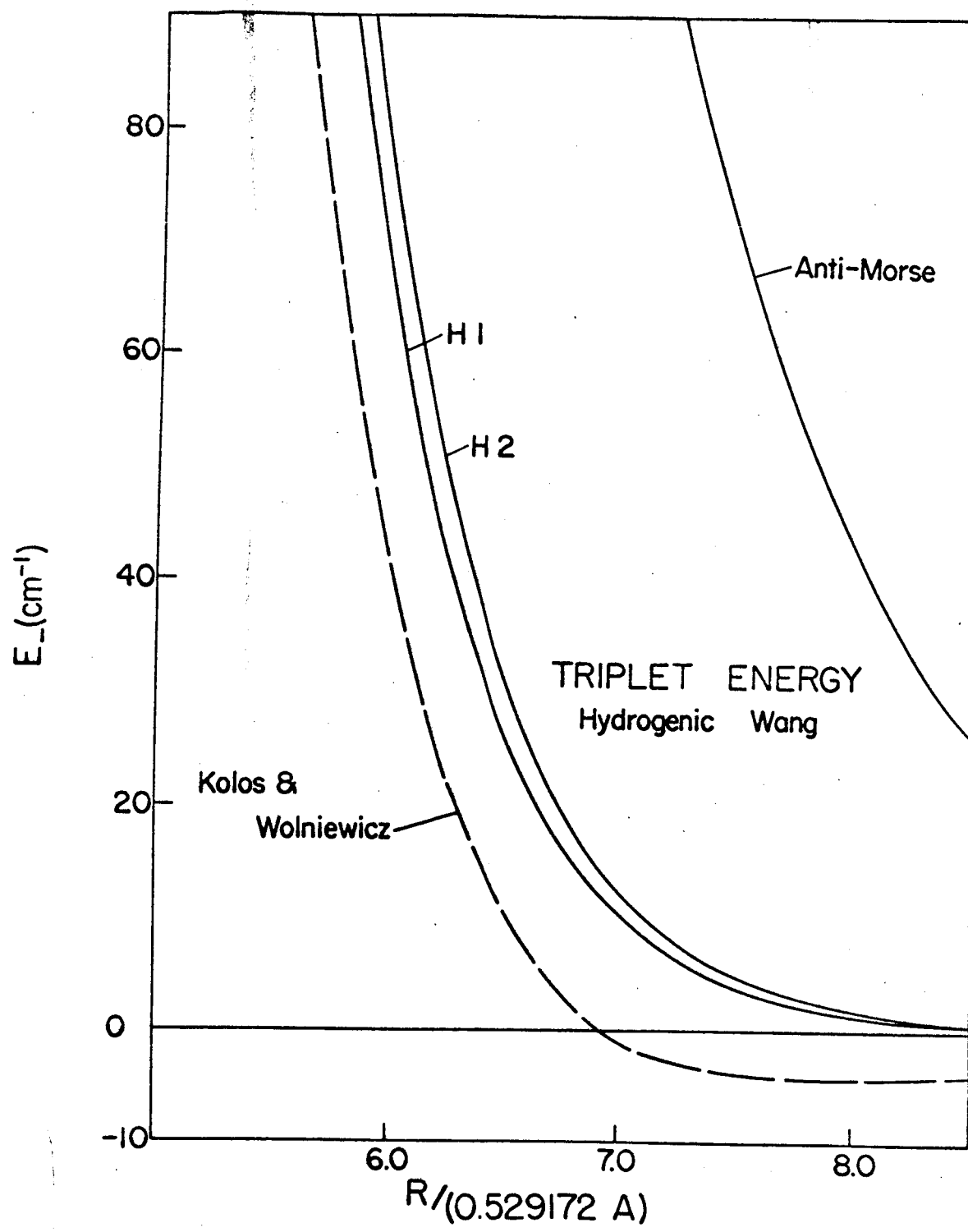


Figure 6

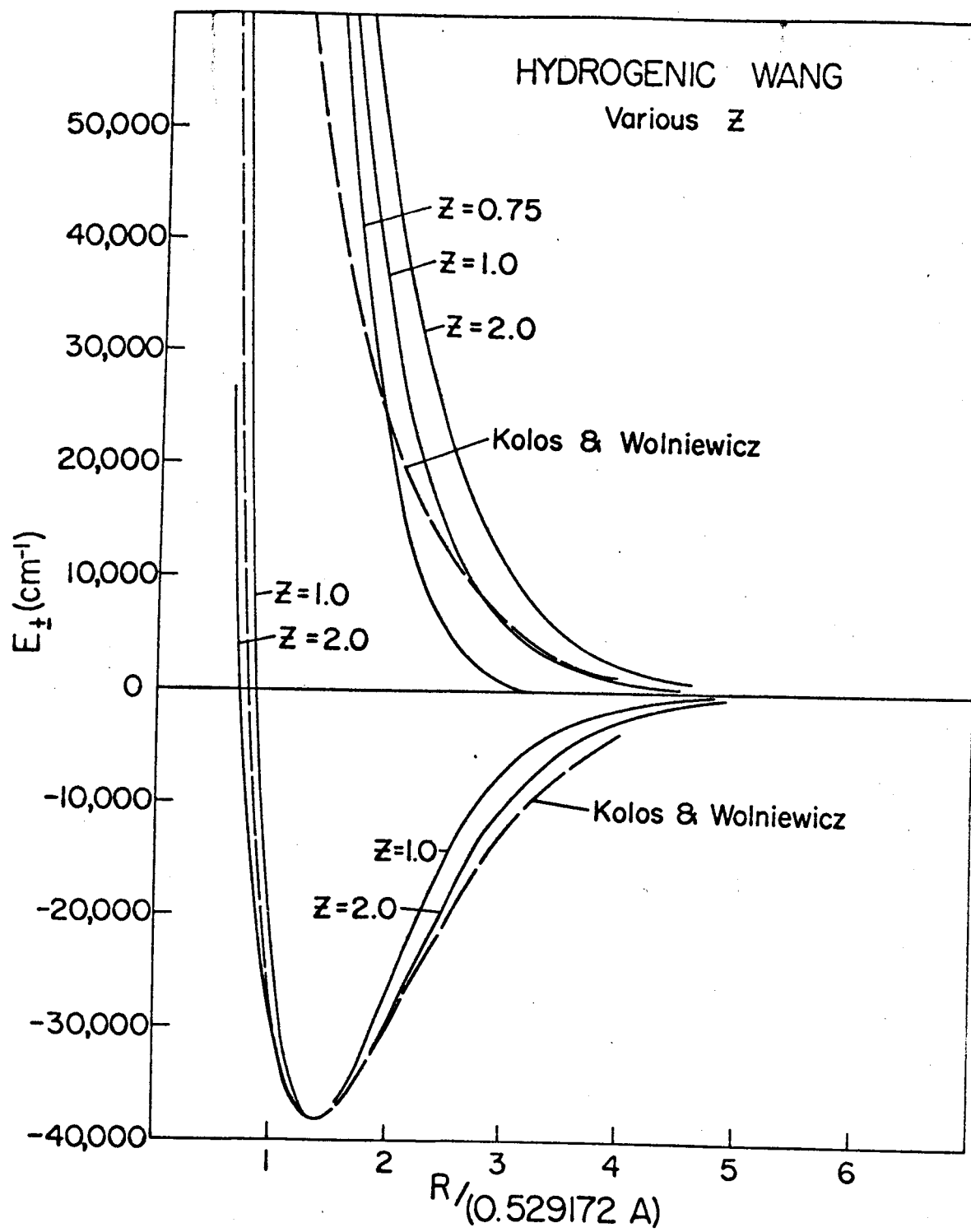


Figure 7

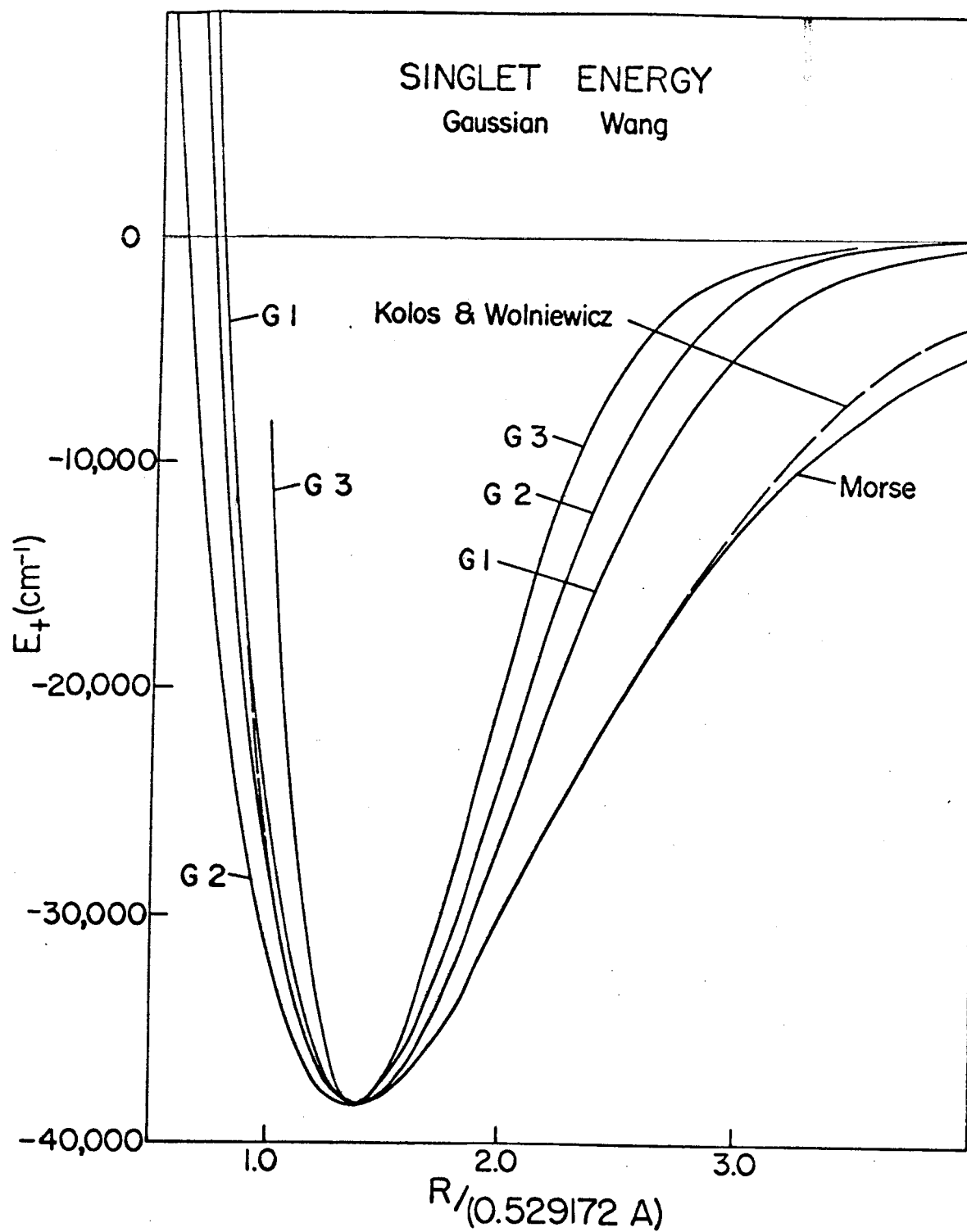


Figure 8

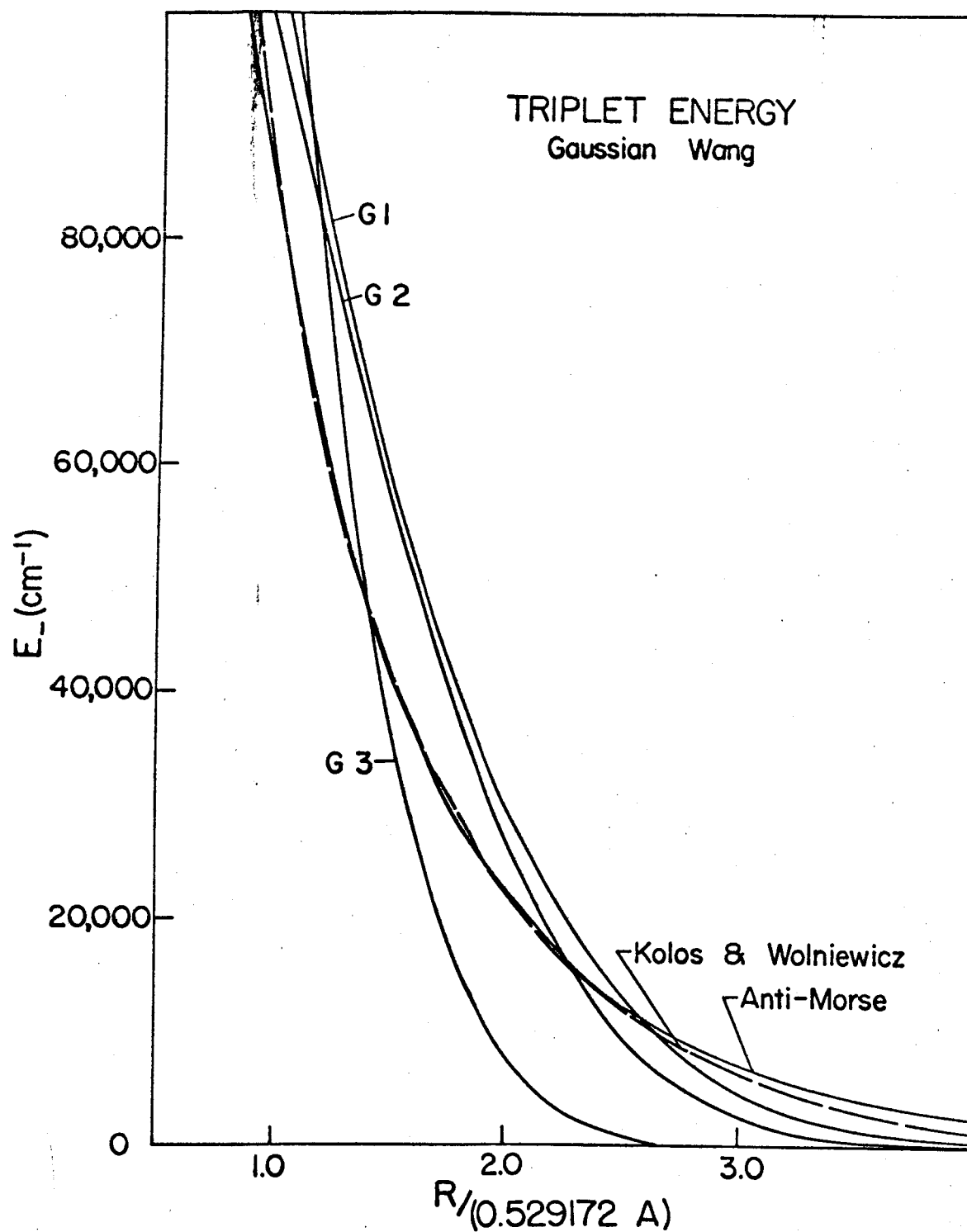


Figure 9

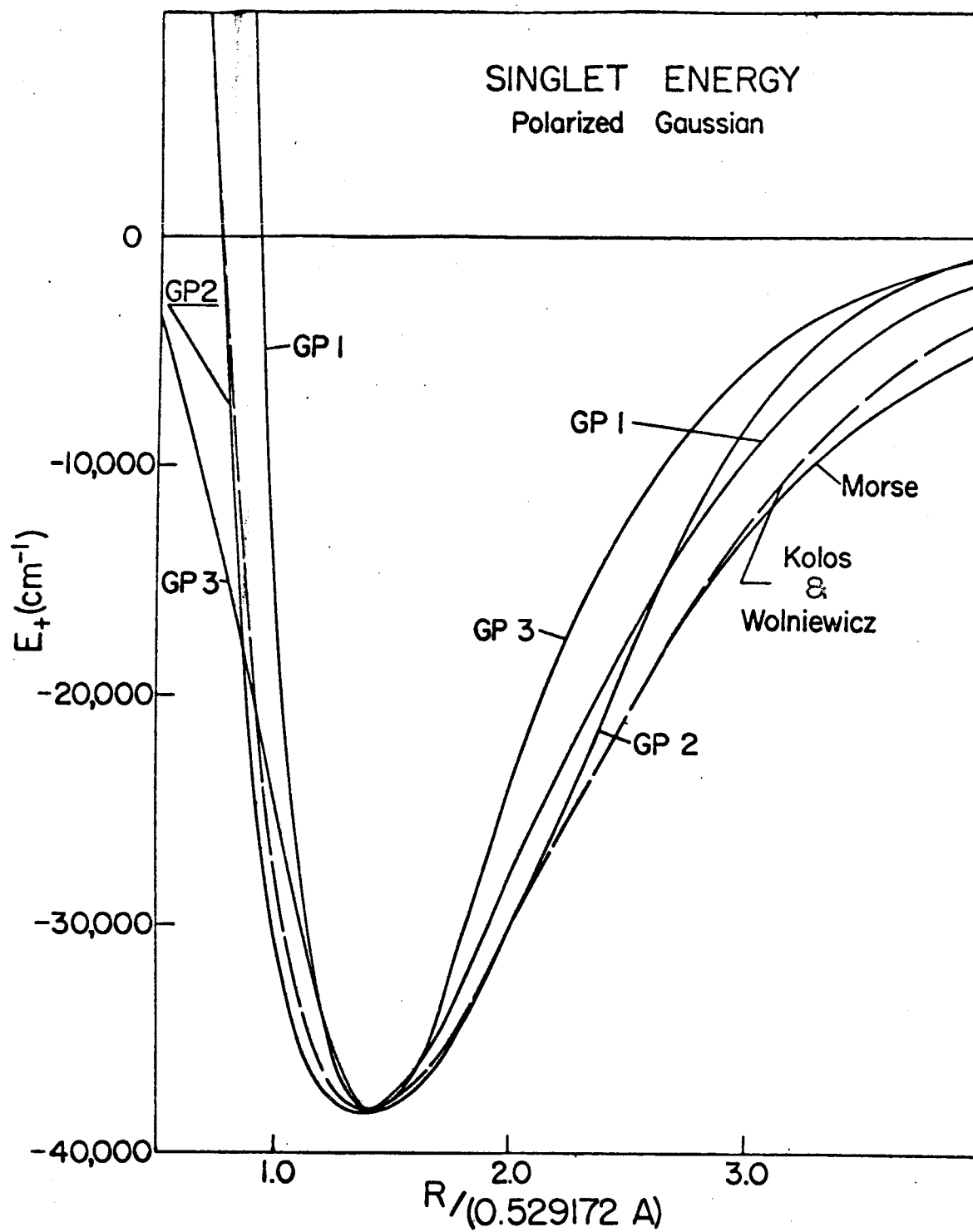


Figure 10

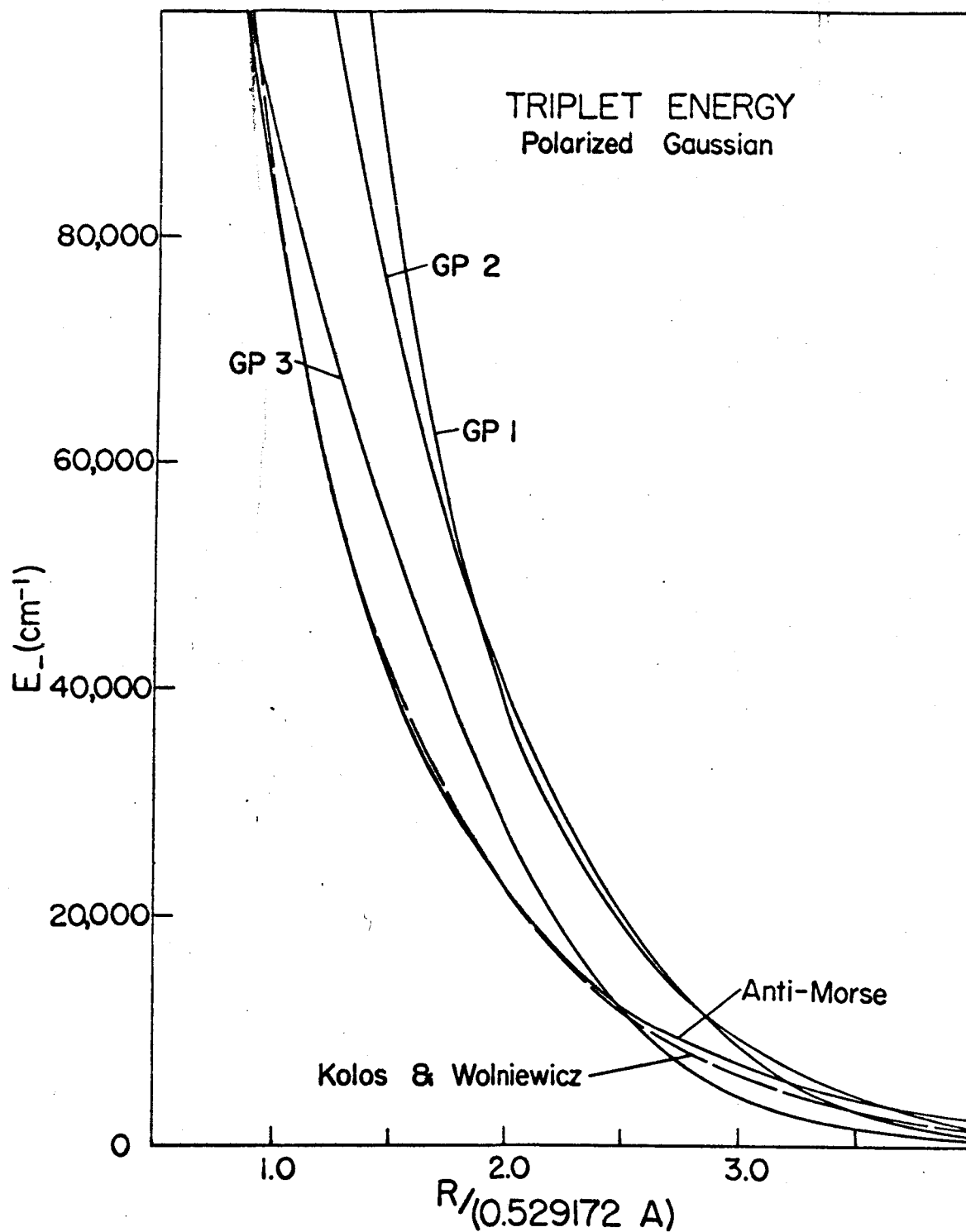


Figure 11

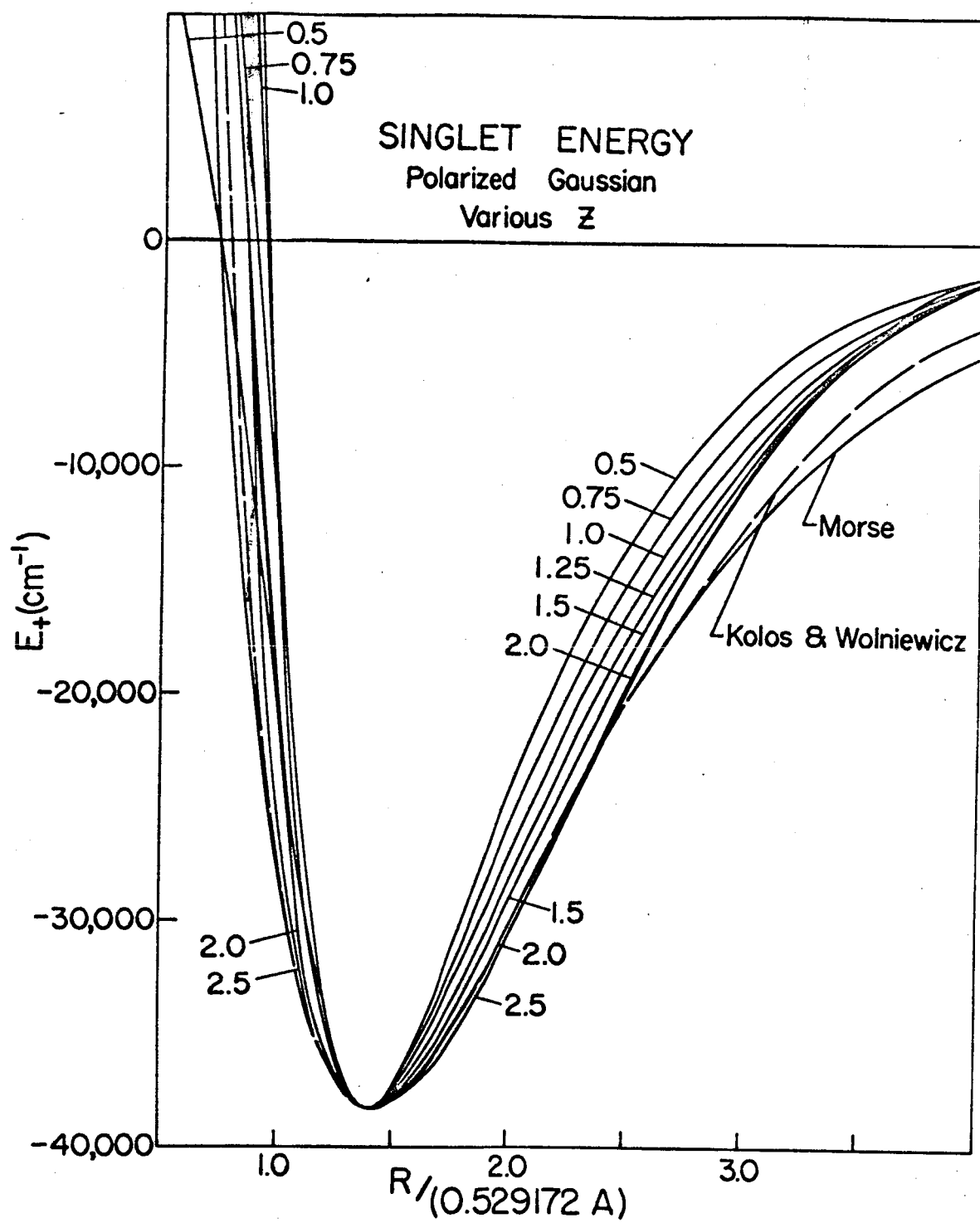


Figure 12

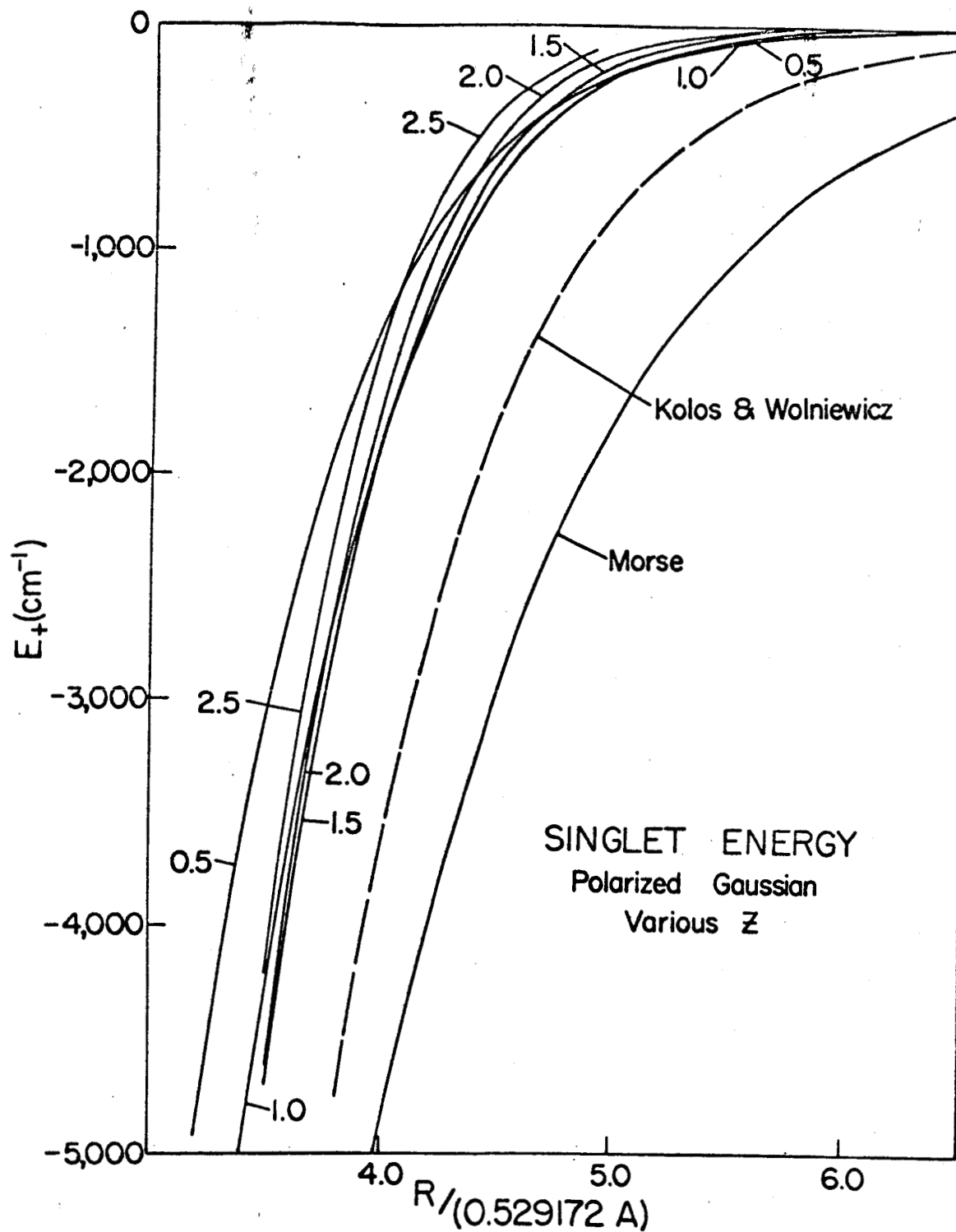


Figure 13

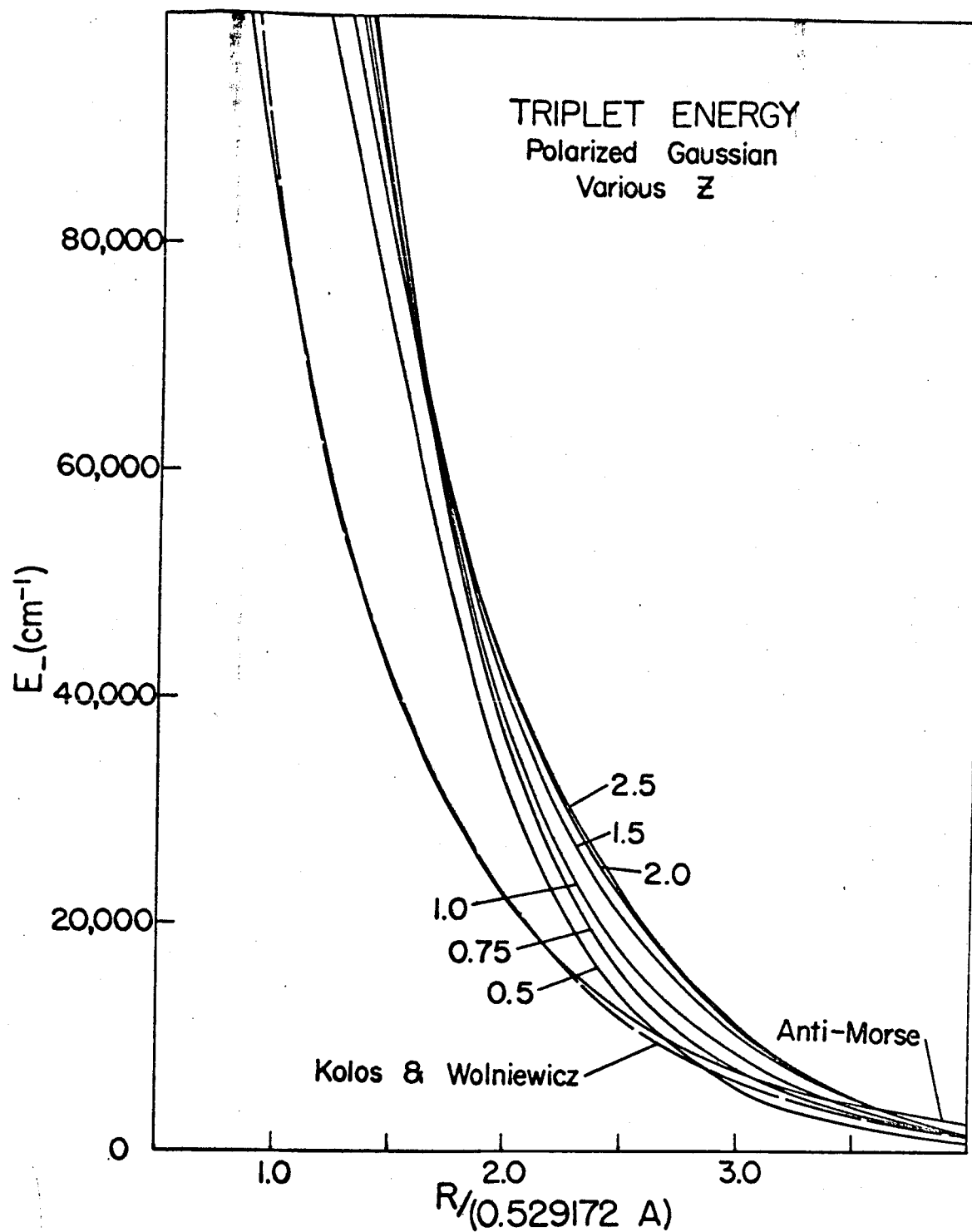


Figure 14

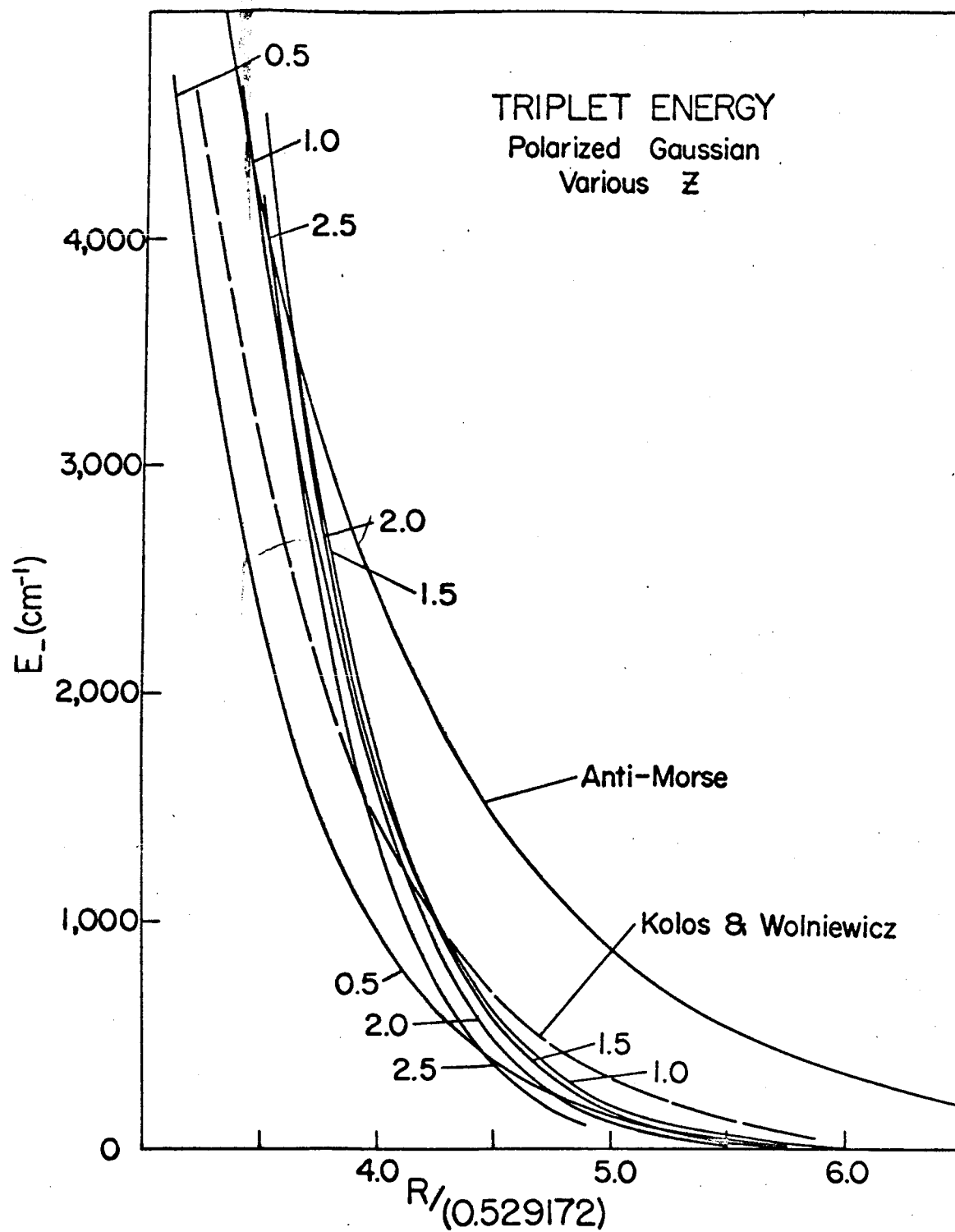


Figure 15

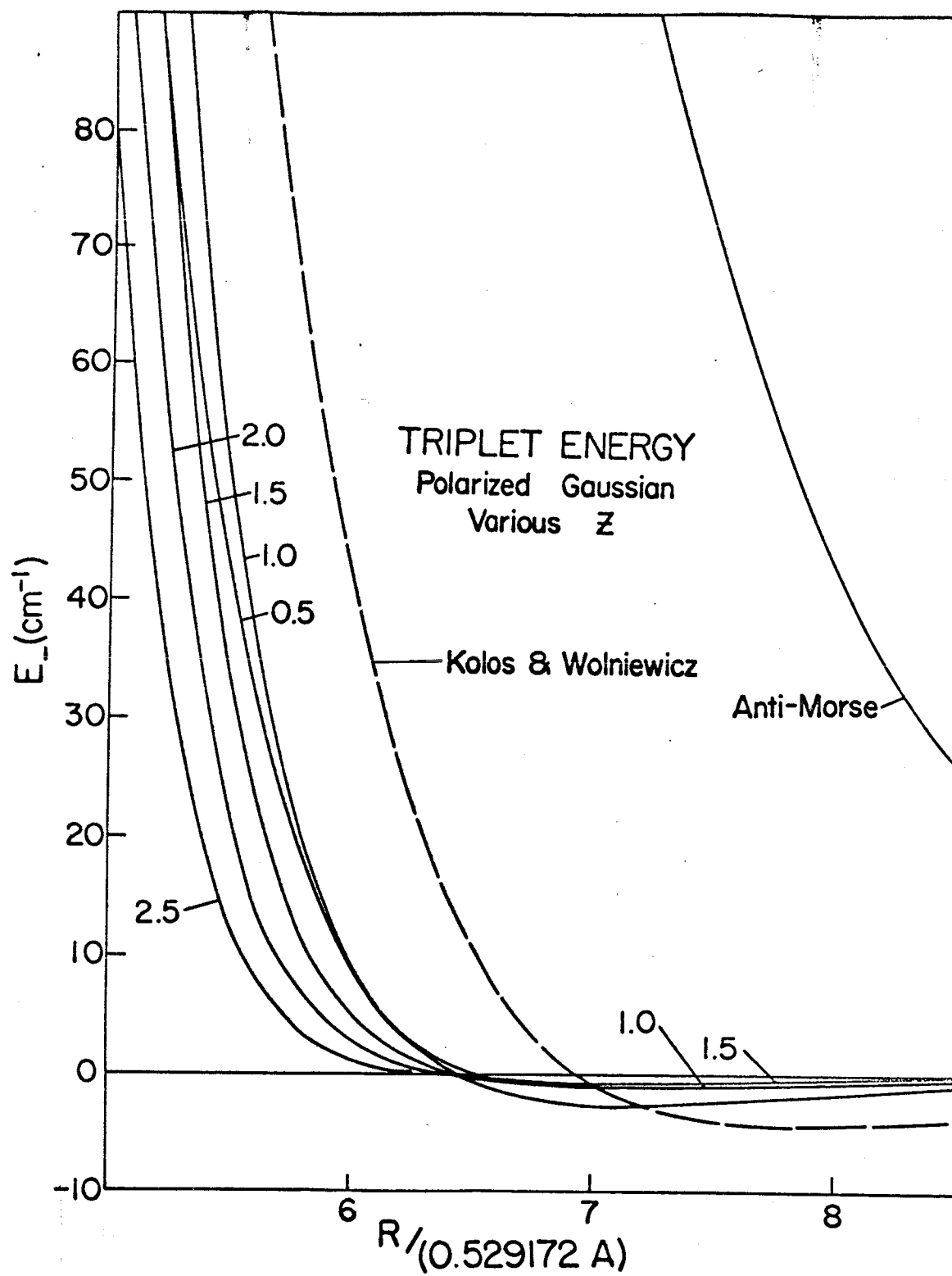


Figure 16

Figure 17

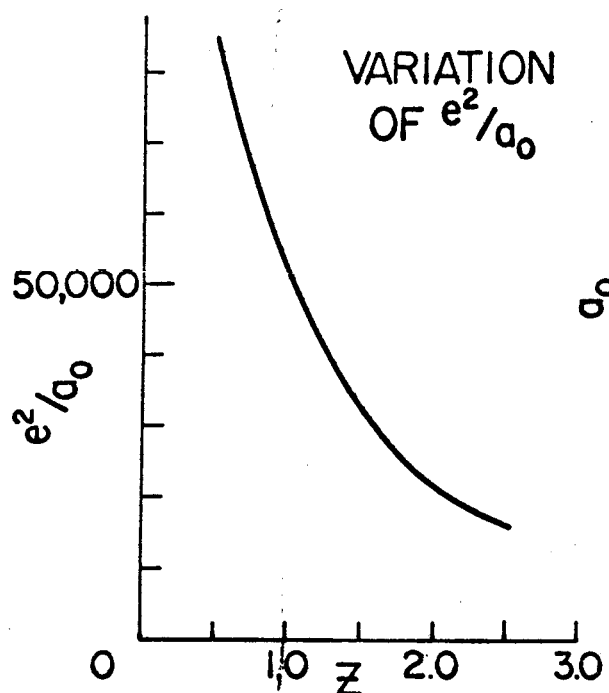


Figure 18

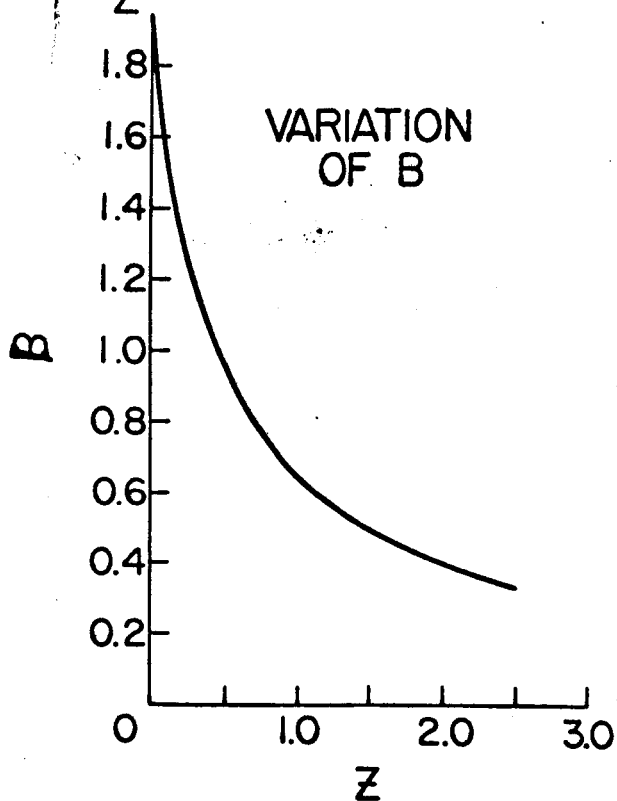
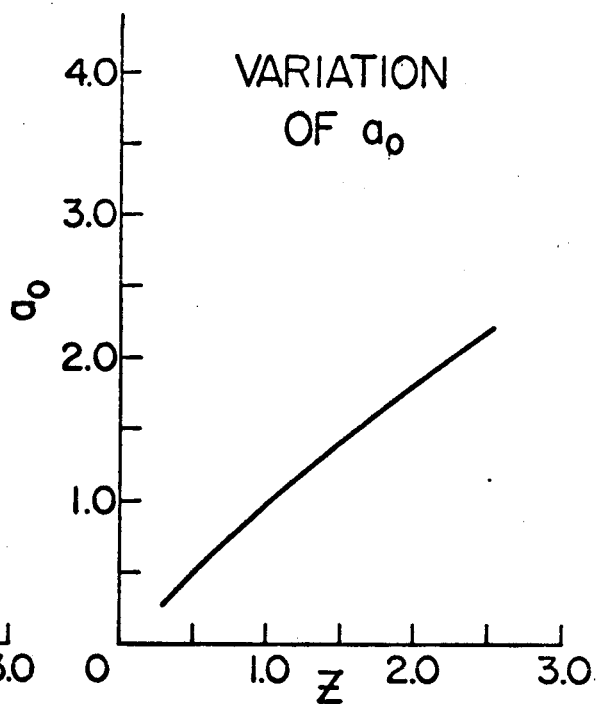


Figure 19

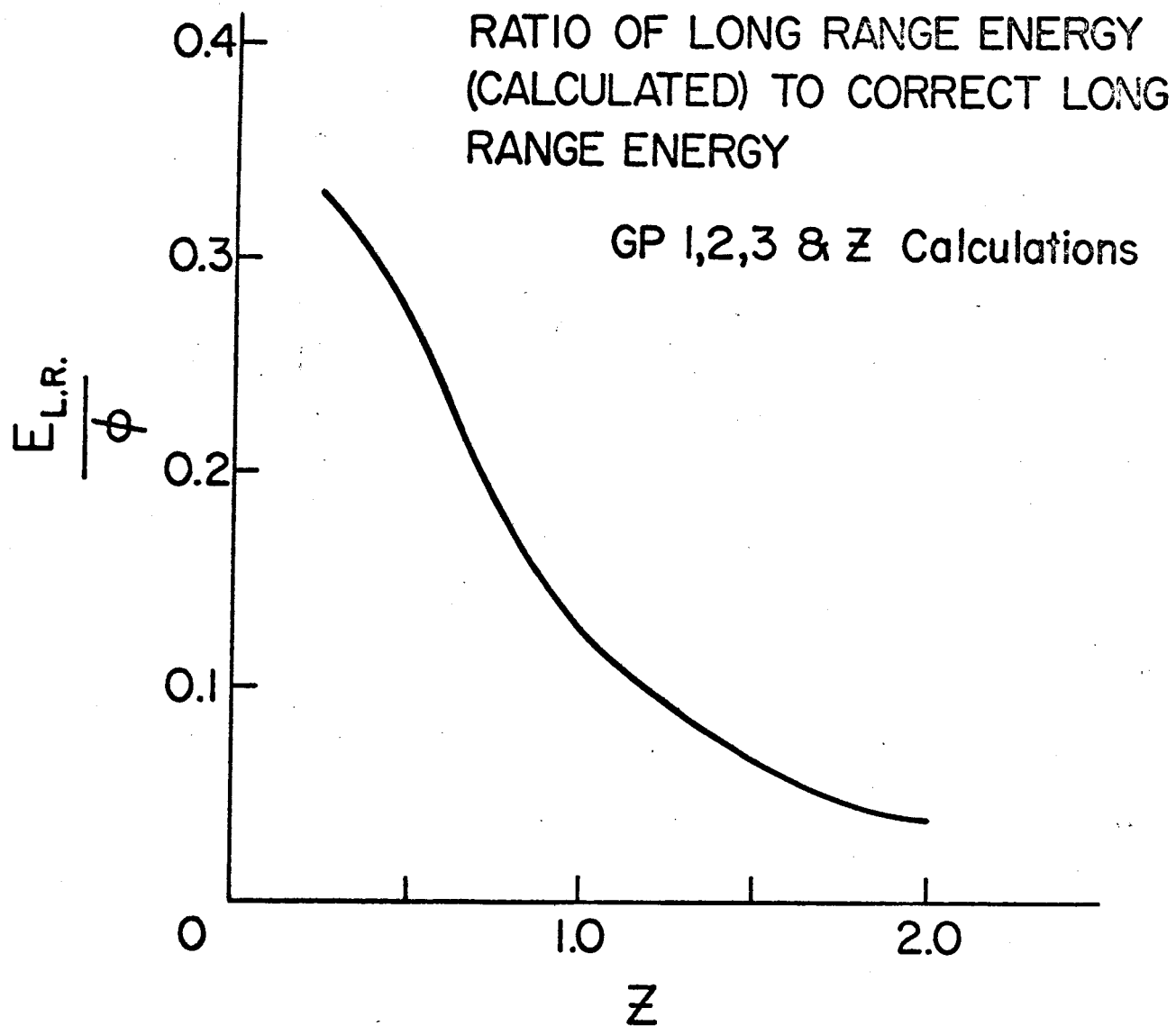


Figure 20